INVESTIGATION INTO THE USE OF POLYPROPYLENE FOR ROTOMOULDING APPLICATIONS

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December 2013

A thesis submitted in partial fulfilment of the requirements of the Manchester Metropolitan University for the degree of Master of Science

Division of Chemistry and the Environment

Faculty of Science and Engineering

Manchester Metropolitan University

DECLARATION

This is a declaration to certify that the material contained in this thesis has not been accepted in substance for any other degree and is not currently submitted in candidature for any other academic award.

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ACKNOWLEDGEMENTS

I would like to take this opportunity to thank Manchester Metropolitan University and Rotomotive.net for giving me the opportunity to carry out this research. Particular thanks and appreciation for the time, advice and support offered by the Professor Herman Potgieter, Dr. Chris Liauw and Dr. Nick Henwood throughout the course and the duration of my stay. I would also like to thank all the technical staff for their help. I am particularly grateful to Peter Luxford who has helped me a lot and it has been a pleasure to work with him.

I am indebted to all the friends made during my English experience.

Finally, and most importantly I would like to thank my parents a my family for supporting me throughout my studies and research.

ABSTRACT

Rotational moulding is a technique employed for processing polymers especially thermoplastics. Rotomoulding (RM) has not been one of the key polymer moulding methods, but it is achieving big interest in the recent years. Rotational moulding is based on the rotation of a mould in two axes and the heating of the material inside an oven. This implies that it is a method without any pressure over the material so, the material would have different properties compared with other moulding methods. During the processing high temperatures are required so, the stabilisation of thermoplastics is almost compulsory. The material which was mainly used with this technique was polyethylene (PE), but recently polypropylene (PP) is attracting the attention of rotomoulders. However, polypropylene is more susceptible to thermo-oxidative degradation due to its structure with a pendant methyl group.

The research has consisted of the analysis of different properties of different polypropylene grades to determine which is the most suitable for rotomoulding processes. The investigation of the mechanical properties such as tensile strength, flexural strength and impact strength has been carried out. The thermo-oxidative degradation of the grades has been also studied by the carbonyl growth after being exposed to high temperatures (230°C). The determination of oxidation induction time (OIT) and oxidation onset temperature (OOT) are also important and all of them are related with crystalline structure of the polymer which was also measured by the heat-cool-heat method of DSC and X-ray diffraction. The analysis of all these properties concludes in the selection of the most suitable grade. However, due to polypropylene weakness to thermal degradation it has to be stabilised.

In an attempt to improve the stabilisation the addition of a primary antioxidant was studied. The antioxidant was part of the hindered phenolic family (Irganox 1010, Penta-erythritol-tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate). The combination with secondary antioxidant such as thioesters (Dioctadecyl 3,3'-thiodipropionate), phosphites (Tris(2,4-di-*tert*-butylphenyl)phosphite) and HALS (Hindered Amine Light Stabilisers) will be studied to see if they can work as synergists. Inorganic controlled release systems were also added because they reduce the mobility of antioxidants due to its high adsorption area. The degradation in PP is mainly caused by oxygen which reacts with the radicals causing chains scissions. The absence of oxygen is supposed to increase polymer stabilization and so the rotomoulding (RM) experiments were also carried out with a N_2 flush. In general these modifications led to improve PP behavior against thermo-oxidative degradation.

OVERVIEW

Chapter 1: It is an introductory chapter in which relevant background information about polypropylene and rotational moulding is discussed. The aim and the objectives to achieve in the research project will be also explained.

Chapter 2: It is included an introduction to the literature which reviews the polypropylene and its structure, as well as the degradation. The materials for its stabilisation are also described in this chapter.

Chapter 3: This chapter explains theoretically the analytical procedures and the processing methods that will be used.

Chapter 4: It describes the properties of the material that will be used throughout the project. The conditions of the experimental procedures and techniques as well as the processing conditions are explained in the chapter.

Chapter 5: The results obtained are presented and discussed in this chapter. The chapter is divided into separate points. The section 5.1 describes the analysis of the properties of different commercial brands and its suitability for rotomoulding. Section 5.2, on the other hand describes and discusses the synergism between stabilisers, the utilisation of nitrogen to improve the stabilisation as well as the difference of heating time to see which combination provides the most suitable data.

Chapter 6: It summarises the results into a series of conclusions reached in this investigation including as well suggestions for further studies that could be carried out from this project.

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1. INTRODUCTION

1.1 BACKGROUND

The term plastic is a general one meant to apply to substances that do not have a fixed melting point. These substances also have a temperature interval where they have flexural and elastic properties, which makes them mouldable into different shapes and makes them useful for multiple applications. However, the correct meaning indicates different synthetic materials obtained by a polymerisation process, resulting in long polymer chains. These synthetic materials are usually petroleum derivatives.

Plastics are generally known as synthetic materials which can be moulded by heat or pressure and are formed by polymers and additives. Polymers are large groupings of monomers joined through a chemical process called polymerisation. With plastics a balance between properties is possible that cannot be obtained with any other material. In fact, plastic refers to a state of the material, not to the material itself. The polymeric materials are synthetic materials that can reach a plastic state. This state is when the material is a fluid with some elasticity, depending on chain length and molecular architectures. The state is usually obtained by thermal heating and it is the stage when the material can be moulded into different shapes and forms. The most common properties of plastic materials are the following: Easy to mould, low production cost, low densities, waterproof, electrical insulating and good chemical resistance.

Plastics can be classified via their base monomer. They can be derived from natural products such as cellulose or rubber or they can be synthetic or derived from petroleum components, i.e. polyethylene or polypropylene. They can also be classified in terms of their behaviour on heating; the latter leads to the thermoplastic and thermosetting classifications. Thermoplastic polymers at ambient temperature are solids and when they are heated above their glass transition temperature or crystalline melting point, they become liquid or a fluid. In contrast to thermoplastics, thermosetting polymers become rigid, due to chemical crosslinking, when they are heated, so reducing the fluidity.

Polypropylene is a synthetic thermoplastic material obtained by the polymerisation of propylene. It is utilized in a wide variety of applications and it can be processed / converted via different moulding / extrusion processes [1].

Since propylene was first polymerised in a stereo-regular manner (to form isotactic polypropylene, from here after designated PP) in 1957 [2], it has been very rapidly adopted as an injection moulding and extrusion material. Whilst rotational moulding (RM) of thermoplastics became established during the 40's and 50's, PP has yet to become firmly established as a rotational moulding material. RM is unique in that it relies on zero-shear sintering of polymer particles in the molten state. In order to allow effective coalescence of the particles (via thermally energised entanglement / interpenetration of chains from neighbouring particles) the polymer must be in the molten state for extended periods relative to other processes such as injection moulding or extrusion. Due to relatively high resistance to chain scission reactions during oxidation and very flexible / rapidly diffusing chains, and low cost, polyethylene (particularly linear medium density polyethylene) has become the material of choice for RM [3].

This investigation will examine the behaviour of a variety of polypropylene samples formulated and different additives combinations for rotational moulding applications.

1.2 PROBLEM STATEMENT

If the thermal stability of PP could be improved, its viability as a rotational moulding material could be enhanced. By virtue of its molecular structure, PP is very unstable and is a good example of a thermoplastic which owes its commercial viability to effective thermal and light stabiliser packages. Whilst the latter are effective enough for extruded and injection moulded products, they are arguably inadequate for RM applications.

1.3 AIM OF THE PROJECT

In this study, the performance of different additives will be compared for a Polypropylene base. The aim is to determine which combination of additives will provide the best long term

thermal-oxidative stability. On other hand, the flushing of nitrogen gas (N_2) inside the mould during the moulding will also be examined to see if that provides some benefits for thermal-oxidative stability.

1.4 OBJECTIVES OF THE PROJECT

The aim of the project will be achieved via the following objectives:

- Characterise the structure and study the mechanical properties of rotational moulding grades of PP currently available.
- Study the effect of the thermal oxidative degradation of the PPs with different stabiliser combinatios added to the PP – this will include one attempt at controlling the release of the stabiliser using an inorganic reservoir / encapsulant.
- Examine the synergism between additives to make PP suitable for rotational moulding.

1.5 HYPOTHESIS

The combination of different additives will provide different performances to the polypropylene base, and yield one with suitable resistance against thermal-oxidation for future rotational moulding applications.

2. LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 POLYPROPYLENE

Polypropylene is currently one of the most prolifically used polyolefins. It was first prepared by the researchers *Giulio Natta* and *Karl Ziegler*. Both found a way to polymerise propylene using a catalyst now referred to as the *"Ziegler-Natta Catalyst".* Both researchers received the Nobel Prize in 1963 for this development.

Different stereochemical forms of polypropylenes can be obtained by this polymerisation system; there are two semi-crystalline varieties and one which is amorphous. The only difference between them is their tacticity. The crystalline varieties are the isotactic and syndiotactic forms and the amorphous variety is atactic. The properties of the isotactic form in particular are better than those of polyethylene (*PE)*. Isotactic polypropylene has quickly found applications in the polymer market. During the 80's it was the third most used polymer, behind only PE and PVC. Nowadays its usage is still growing faster than that of any of the others polymers. It is currently produced using a Ziegler-Natta, and more recently, *Metallocene-Catalysis* [4].

The monomer is obtained from the petroleum industry in the same way as PE by a *"Cracking Process"* which yields a mixture of propane and propylene. These two compounds are then separated by distillation. Different additives can be added to polypropylene, for example fillers to change its properties, e.g. talc, fibreglass or calcium carbonate. When properly coupled to the matrix, the former filler in particular can substantially increase the strength and stiffness of PP and is therefore classed as a reinforcing filler, whilst the latter mainly improves stiffness and reduces mould shrinkage in an isotropic manner.

Usually PP applications are compared with those of PE. However, since it is produced by injection moulding, it is useful to compare PP with other polymers. For example, polystyrene (PS) and Cellulose Acetate are as rigid as PP. The next table (Table 2.1) shows some general comparisons.

When low density, chemical resistance and high softening point are required for a component, PP is often turned out to be the polymer of choice. PP is also used for making thin films for packaging applications by virtue of its flexibility and degradation resistance, when properly stabilised. PP is used for, among other things, for suitcases, automotive components, washing-machine components, etc. The poor low temperature impact strength of PP can be countered by copolymerisation with ethane and by bleding with olefinic thermoplastic elastomers and used to make ski-boots and car bumpers.

Table 2.1: Comparison of the relative properties for some commodity thermoplastics [5].

Polymer	**Clarity of moulding**	**Temperature resistance**	**Toughness**
Polypropylene (homopolymer)	opaque	A	F-G
Polypropylene (copolymer)	opaque	B	D-F
Polyethylene (high density)	opaque	D	D-F
Polystyrene	clear	E	H
High-impact polystyrene	opaque	F	D-G
ABS polymers	opaque	C	A
Cellulose acetate	clear	G	B-C

Note: Letters indicate the relative quality of a particular property; A, for excellent, to H, for very poor.

2.1.1 Tacticity

Polypropylene has an asymmetric carbon atom in each repeat unit. The size of the methyl group is sufficient to render the planar zig-zag conformation energetically unfavourable. In order to maximise the distance between methyl groups the main chain bonds rotate, resulting in a helical conformation. Regular patterns of stereochemistry of the asymmetric carbon atoms result in regular helices which are able to pack into a crystal lattice. This allows the formation of three different tactic forms, which result from these structural stereochemical isomers.

The pendant methyl group is what gives PP its special characteristics. If the group was changed for hydrogen, as in PE, or by a chloride like in PVC, its properties would have been totally different.

Polypropylene can be isotactic, syndiotactic or atactic, depending on the orientation of the pendant methyl group. In the isotatic form pendant methyl groups are all in the same configuration and all on the same side of the polymer backbone. Due to this regular configuration, isotactic PP has the highest crystallinity of the three tactic types. Because of its mechanical, physical and thermal properties, this is the most common and utilised form of PP.

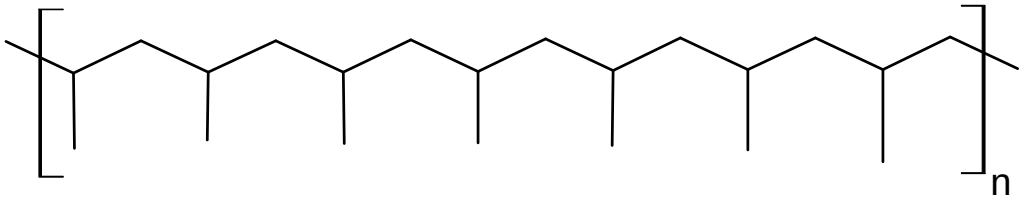


Figure 2.1: Skeletal representation of isotactic polypropylene (iPP). All the pendant methyl groups point in the same direction.

In syndiotactic PP, adjacent pendant methyl groups are orientated in the opposite direction of their nearest pendant methyl group. Some properties are different when compared to isotactic PP, such as lower crystallinity and stiffness. However, syndiotactic PP has better impact strength and clarity than the isotactic form.

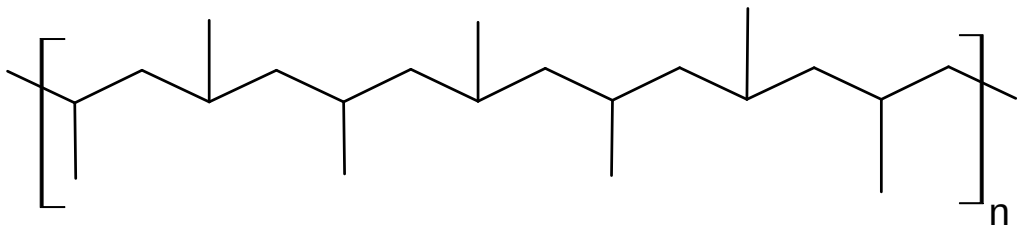


Figure 2.2: Skeletal representation of syndiotactic polypropylene (sPP). The pendant methyl groups point in alternative directions away from the PP backbone.

In the atactic form, pendant methyl groups are configured randomly on opposite sides of the backbone. Due to its irregular configuration, giving a knobbly irregular helix, this structure

shows little crystallinity (between 5% - 10%), so it will be soft, flexible and easily dissolve in aliphatic and aromatic hydrocarbons at ambient temperature. The most common application for atactic PP is to use it in adhesives due to its sticky, amorphous nature. [6]

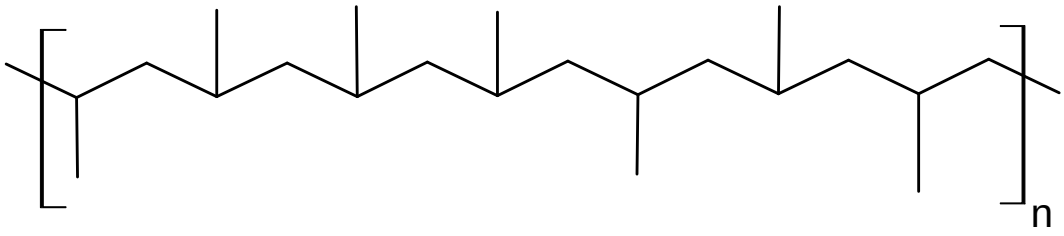


Figure 2.3: Skeletal representation of atactic polypropylene (aPP). Pendant methyl groups point alternatively randomly away from the PP backbone.

2.1.2 Polymerisation Processes

Polymerization is a chemical reaction in which monomer molecules combine to form a polymer. There are two polymerization methods, which are very different from each other. One is called addition-polymerization, while the other one is condensation-polymerization. PE and PP are classic examples of addition polymers.

In addition-polymerisation there are serial reactions where each reaction increases the chain length by one repeat unit whilst retaining the active centre. The active centre can be a free radical or an ionic species (anion or cation). These serial additions of monomers of the growing chain result in a macromolecule being produced. If the active centre is a free radical, the growing chain is known as a macroradical.

Polymerisation implies the addition of a free radical to the double bond of the monomer molecule. This happens during propagation. However, it is first necessary to create the free radical. To make it possible, an initiator is required. Initiators typically contain molecules which have some weak bonds that could be broken by a very low quantity of energy, such as peroxide bonds [7, 8].

Ziegler-Natta catalysts, greatly increase the controllability of ethane and propene polymerisation in reactions. Those catalysts are made of salts of some typical metals such as

titanium or zirconium. Furthermore, these catalysts make PE or PP chains longer and more regular, so some properties, such as toughness and strength, are improved. The application of these catalysts enables much greater control over the stereochemistry, linearity and length of the polymer chains produced.

2.1.2.1 Ziegler-Natta Catalyst

Ziegler-Natta catalysts have great interest in the polymerisation of propene, so they need special mention in this chapter. The development of a catalyst for polypropylene polymerisation in the 1950's made the production of stereospecific polypropylene possible and led to the rapid growth rate of PP that is still continuing today. Catalysts are substances that increase the rate of a reaction but without any changes in their molecular structure. In polypropylene polymerisation catalysts are organometallic transition metal complexes. They provide active sites where the polymerisation occurs, by holding both the growing polymer chain and the reacting monomer close to each other. [7]

At first, these catalyst were prepared by reducing high valence metal compounds, like $TiCl_4$, with organometallic compounds like $Al(C_2H_5)$, but this process obtained less than 50% of isotactic fractions. Later, highly hetereogeneous catalysts based on transition metals, with a valency of three or less, such as $TiCl_2$, $TiCl_3$, $ZrCl_3$, and VCl_3 were developed to obtain stereospecific polypropylene. The metal halides were combined with selected metal alkyls. The resultant catalyst yielded crystalline polypropylene with high fractions of iPP with an atatic impurity minimised to nearlly 5% [6]. However, the products also contained some low molecular weight fractions, hence they still need purification and separations to obtain relatively pure iPP. Natta also discovered that the addition of Lewis bases enhances the quantity of crystalline material [9]. Table 2.2 shows the effects of the addition of Lewis bases.

Table 2.2: Effect of addition of Lewis Base on the amount of crystalline fraction in polypropylene [9].

Transition Metal Halides	**Aluminium Alkyl**	**Lewis Base**	**% Crystallinity**
$TiCl_3$	$2Al(C_2H_5)Br_2$	Pyridine	>98.5
$TiCl_3$	$2Al(C_2H_5)Cl_2$	$N(C_2H_5)_3$	95
$TiCl_3$	$2Al(C_2H_5)Cl_2$	$NH(C_2H_5)_2$	93
$TiCl_3$	$2Al(C_2H_5)Br_2$	$N^+(C_4H_9)_4I^-$	>99
$TiCl_3$	$2Al(C_2H_5)Cl_2$	$N^+(C_4H_9)_4Br^-$	96

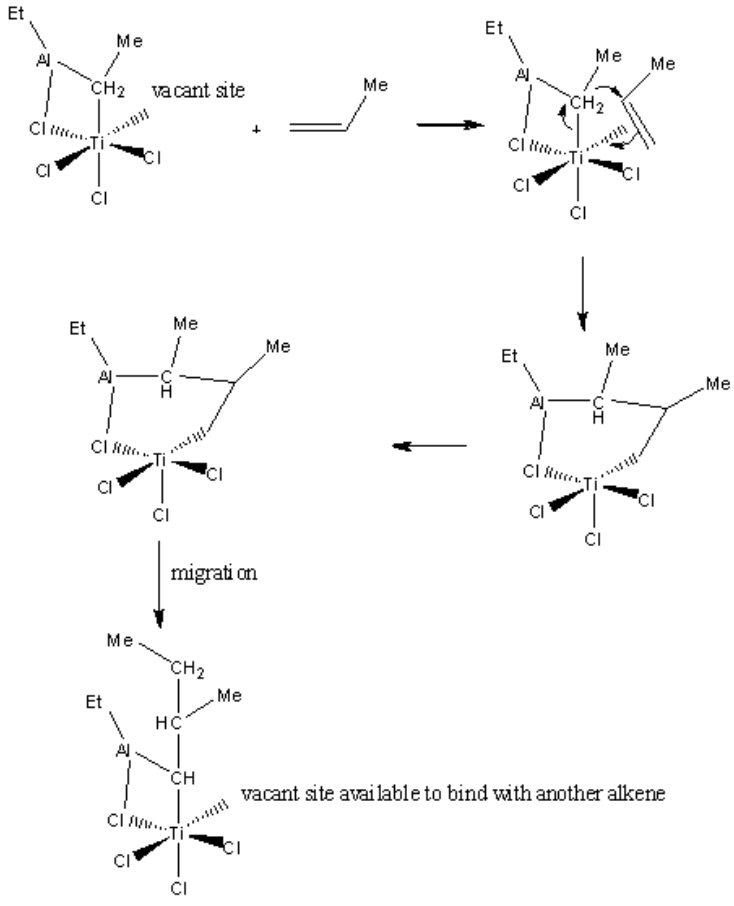


Figure 2.5: Schematic illustration of the mechanism of Ziegler-Natta catalyst for PP polymerisation [11].

2.1.2.2 Metallocene Catalysts

Metallocene catalysts have recently been developed for industrial use. In contrast to Ziegler-Natta catalysts, metallocene catalysts are single-site and they have received widespread attention due to their ability to increase control over tacticity and molecular weight distribution.

Metallocenes are organometalic compounds with a sandwich-spatial arrangement, consisting of a transition metal situated between two cyclic organic compounds [7]. The nature of the transition metal and the structure of the ligand have a large effect on its catalyst behaviour. The shape, geometry, and chemical structure of the ligand can affect the activity and selectivity of the catalyst. The symmetry imposed by ligands around the active site determines the geometry for monomer coordination and consequently the orientation of the catalyst growing polymer chain.

Metallocene catalysts offer a narrow molecular weight distribution. Metallocenes are more sensitive to hydrogen that Ziegler-Natta catalysts, which result in the ability to produce high melt flow rate polymers. In conclusion, metallocene catalysts are more effective than conventional catalysts for incorporating high levels of a wide variety of olefin comonomers. Commercial metallocene catalysts demonstrate high catalytic efficiency, and this efficacy has been proven in a variety of commercial processes, including solution, slurry, gas-phase and high pressure bulk polymerisations [10].

2.1.2.3 Slurry Process Polymerisation

After the discovery of the Ziegler-Natta catalyst, polymerisation of polypropylene began commercially. One of the first processes was a slurry polymerisation process. In slurry polymerisation, chain growth occurs as monomers dissolved in a hydrocarbon solvent (butane, heptane, hexane) which is added to growing chains, also dissolved in the solvent. Two fractions result from the polymerisation: one fraction is soluble in the solvent, while the other is not. These two fractions are separated by centrifugation, thereby creating two products streams. The insoluble fraction creates a slurry phase and is predominately isotactic material. The

soluble materials are low molecular weight oligomer materials or highly atactic PP that precipitates from solution when the solvent is boiled off at high temperatures. The unreacted monomer is also released as gas when the solvent boils off [12].

Slurry processing plants are large with lots of expensive equipment which made them inefficient. Furthermore, environmental and safety issues arose due to the large volumes of solvent and amorphous waste products. In time, plants benefitted from improved stereo-specific catalyst and evolved to more advance slurry methods in late seventies [6].

2.1.3. Oxidative Degradation of the Polypropylene

Degradation is one important factor that must be analysed and understood for practical applications. Polymers are exposed to multiple degradative agents during processing, treatment and storage. Chemical, physical and biological reactions could cause changes in polymer properties usually by crosslinking and/or chain scission. Mechanical, optical, electrical properties could change. All the transformations in the properties are called degradation. The desirable properties of the polymers are generally due to their long chains, hence changes in length/architecture of in the chains would result in deleterious effects on the material [13].

Polymers used in outdoor applications are subjected to a range of degradation agents including: UV radiation, elevated temperatures, mechanical forces and atmospheric pollutants. All of these combine with atmospheric oxygen and cause oxidation to occur via a range of routes, each being initiated via a different mechanism. Furthermore, during processing polymers are exposed to high temperature and pressure plus dissolved oxygen.

Chemical transformations in polymers follow three steps. First of all, active species have to be created during an initiation process. The second step is the propagation where the degradation reactions occur. The third step is termination where active species become inactive products. The three steps could occur by different degradation processes, but in this project thermal-

oxidative degradation, which occurs during processing or use at elevated temperature, is the only route that will be explored in detail.

On exposure to oxygen, and heat, oxidation of the polymer may occur. The extent and mechanism of oxidation is heavily dependent on the structure of the polymer. From a theoretical point of view, most commercial polymeric systems should be relatively stable above their melting point in the absence of oxygen. However, in the presence of oxygen most polymers will undergo rapid chain scission and/or crosslinking reactions below their melting point [14].

During this project PP is the polymer to be investigated. The oxidation in PP in the presence of oxygen occurs more rapidly than in PE because of the pendant methyl group. PE, polyisoprene and PP behave more or less in the same way because the three of them are similar carbon-hydrogen type polymers known as polyolefins or polydienes. In general, these types of polymers are very susceptible to thermal degradation [15].

2.1.3.1 Initiation

Initiation might occur as a spontaneous result of mechanical shear, impurities and the absorption of heat or ultra-violet light. However, PP is oxidised or degraded differently. Some of these control factors could be the following: oxygen pressure, temperature, initiation rate, sample thickness, stretch ratio, etc. [6, 16]

This spontaneous result is often initiated by a free radical propagation progress and it is thought that the main reason for formation of radicals is the weakness between C-C and C-H bonds, especially in PP, even though they are stable at normal conditions and they should not break unless there is an exoergic process or an impurity. Due to its pendant methyl group and the tertiary hydrogen atom, the formation of radicals is even more probable.

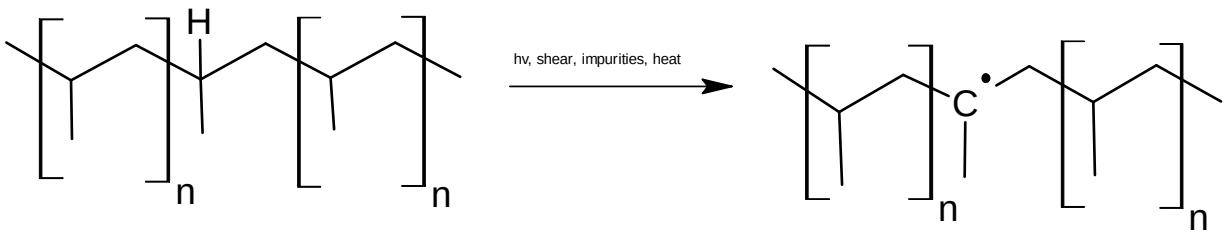


Figure 2.6: Initiation step showing radical formation in PP chain via abstraction of tertiary hydrogen atom.

The initiation step involves the formation of an active site which is caused by the proximity of a free radical. The identity of the initiator is not often discussed in detail because it is not really relevant and there are a large variety of initiators. The initiation involves the hydrogen atom from a tertiary carbon in the case of PP. At high temperatures the homolytic fission of a C-C bond could also result in the formation of macroradicals. The oxygen molecule it is also a potential initiator of thermal-oxidative degradation at temperatures above 500°C [17].

2.1.3.2 Propagation

The proximity of diradical oxygen molecules results in a reaction with the free radical of the polymer backbone. The resultant product, often a new radical with the structure of unstable hydroperoxide, is formed. Because of their instability they continue reacting with weak C-H bonds to form hydroperoxides and a new free radical in the PP backbone [7].

The propagation step is limited to amorphous regions of PP where the oxygen diffusion rate is the greatest. During the oxidation the rate of oxygen uptake into the polymer is inversely proportional to the crystallinity content of the polymer. Thus the atactic polymers will be less resistant to oxidation than isotactic types [18].

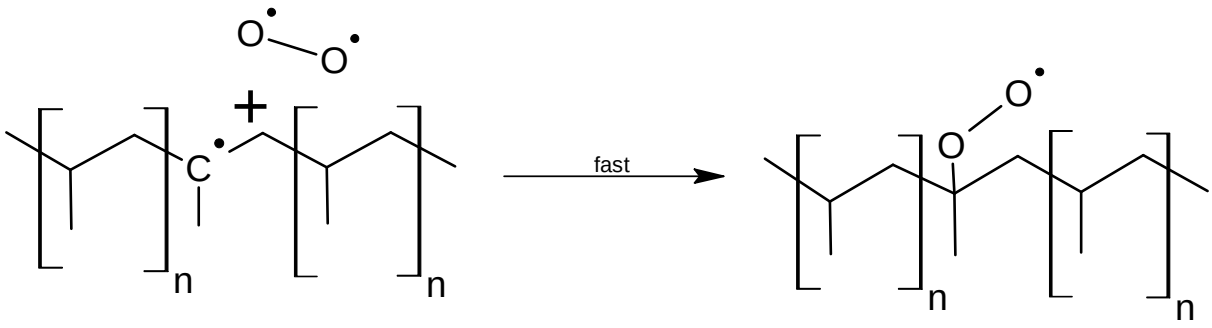


Figure 2.7: Propagation step showing the formation of unstable peroxy radicals.

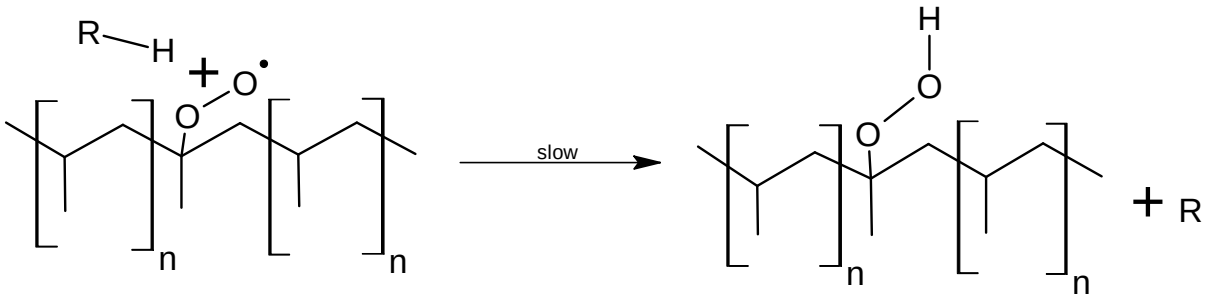


Figure 2.8: Propagation step showing the resultant formation of stable hydroperoxides.

2.1.3.3 <u>Termination</u>

The termination step results in the union of two free radical species (alkyl, alkoxy or peroxy). They also can be united with atomic hydrogen. This causes an increase in the molar mass of PP backbone.

$$R\cdot + R\cdot \longrightarrow R\text{-}R$$

$$RO\cdot + RO\cdot \longrightarrow ROOR$$

$$ROO\cdot + ROO\cdot \longrightarrow ROOR + O_2$$

Figure 2.9: Termination reactions eliminating radicals.

2.1.3.4 Branching

Hydroperoxides are degradation products formed in polypropylene and they can also be decomposed or degraded into new species because of heat, light, shear or the presence of metal ions. Some of these species are alkoxy and hydroxyl radicals, which can develop in chain transfer reactions to form new radical species to encourage the propagation cycle. Due to the continuous formation of hydroperoxides on the polymer backbone during the propagation step and then followed by the branching step, degradation in polypropylene is considered an auto-catalytic process [19 - 22].

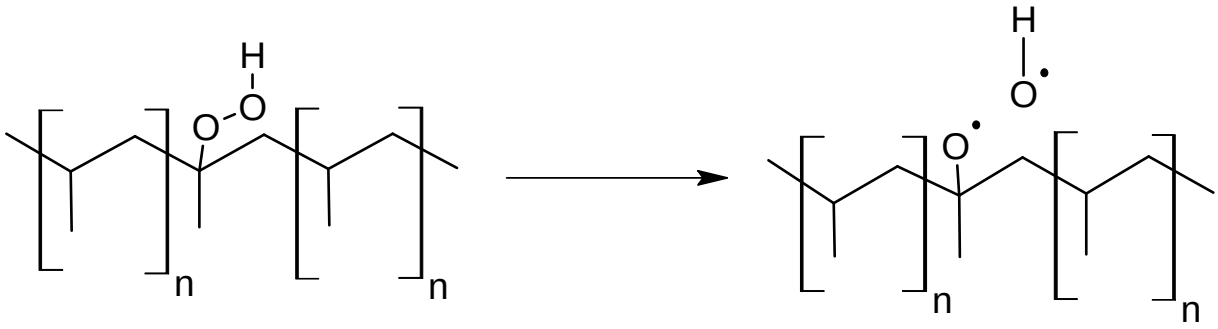


Figure 2.10: Decomposition of hydroperoxide.

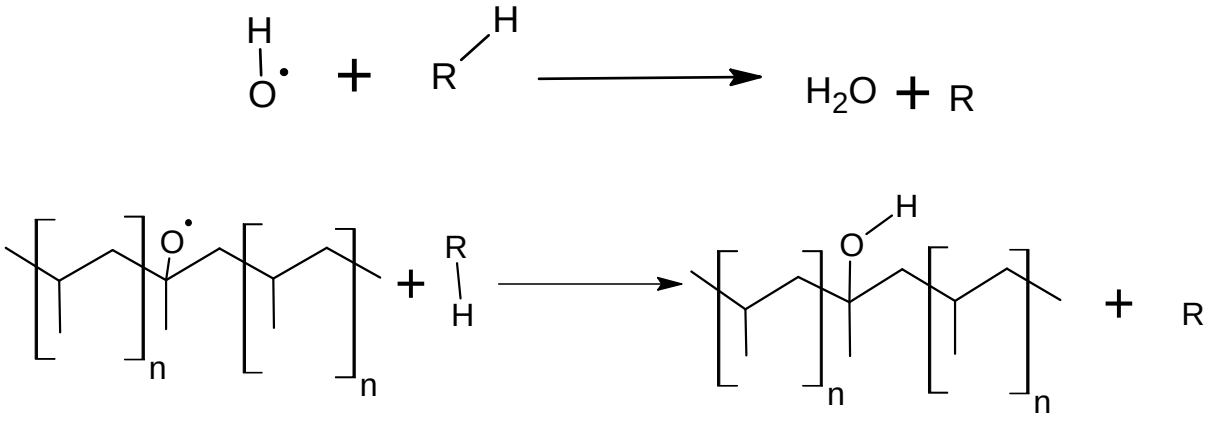


Figure 2.11: Chain transfer reaction during branching step.

2.1.3.5 Additional Reactions of Degradation Products

Apart from the oxidation step described above, new compounds are formed during the degradation of the polymer, especially during thermal oxidation. Thermal oxidation refers to the exposure of heat in an environment containing molecular oxygen or ozone.

As polypropylene has a tertiary hydrogen atom bonded to the backbone, oxidation occur much easier than in polyethylene. It could be so susceptible that polypropylene could start to degrade even at room temperature. Degradation products are formed on the surface of the polymer and in the amorphous regions of the polymer where oxygen can react with free radicals. Degradation becomes more rapid when the polymer is in the melt state whilst exposed to high shear such as encountered during extrusion, blow moulding and injection moulding. During these processes the following reactions and products have been found:

- ***Alkoxy Radicals:***

Alkoxy radicals are formed during the branching step of the oxidation. They can develop several different reactions. Some of the most relevant are β-scission and hydrogen abstraction.

Alkoxy radicals are one the major species which led to chain scission, as can be seen in β-scission reactions. The reaction can be performed by secondary and tertiary alkoxy radicals, but in the case of polypropylene tertiary types predominate. Unimolecular β-scissions can separate the polymer backbone in two smaller parts or they can even produce a methyl radical which may dimerise to ethane.

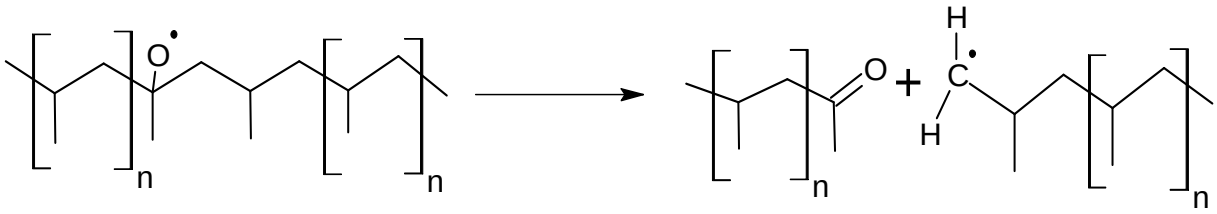


Figure 2.12: Unimolecular decomposition of tertiary alkoxy radicals (β-scission).

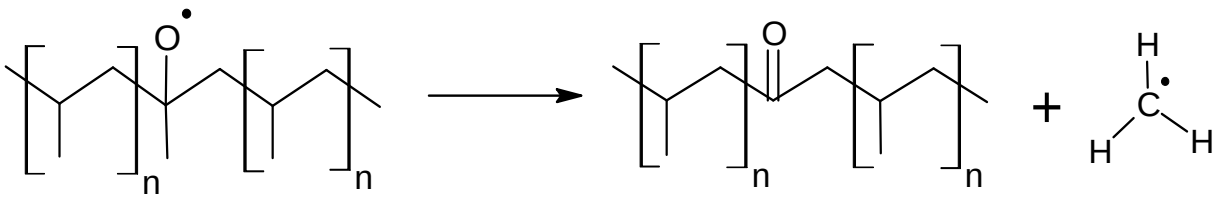


Figure 2.13: Unimolecular decomposition of tertiary alkoxy radical to procuce a ketone and a methyl radical.

Furthermore, an alkoxy radical can be stabilised with the elimination of hydrogen. These eliminations could occur from primary, secondary and tertiary positions. However, intramolecular eliminations are preferred which are called isomerisation reactions. The most common intramolecular reactions are 1,5-hydrogen elimination and 1,6-hydrogen elimination due to the relatively stable species formed. During the hydrogen transition the transition state is a five member or six member ring, depending on the highest steric stability. Other reactions can also occur when a tertiary alkoxy is adjacent to a tertiary alkyl, e.g. decomposition and oxidation [23].

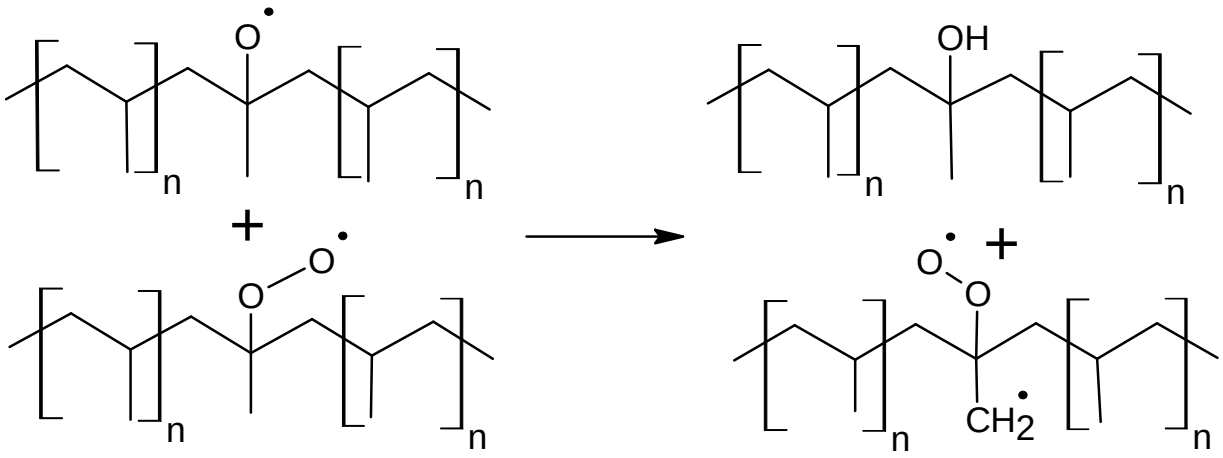


Figure 2.14: Primary hydrogen elimination from an alkoxy radical.

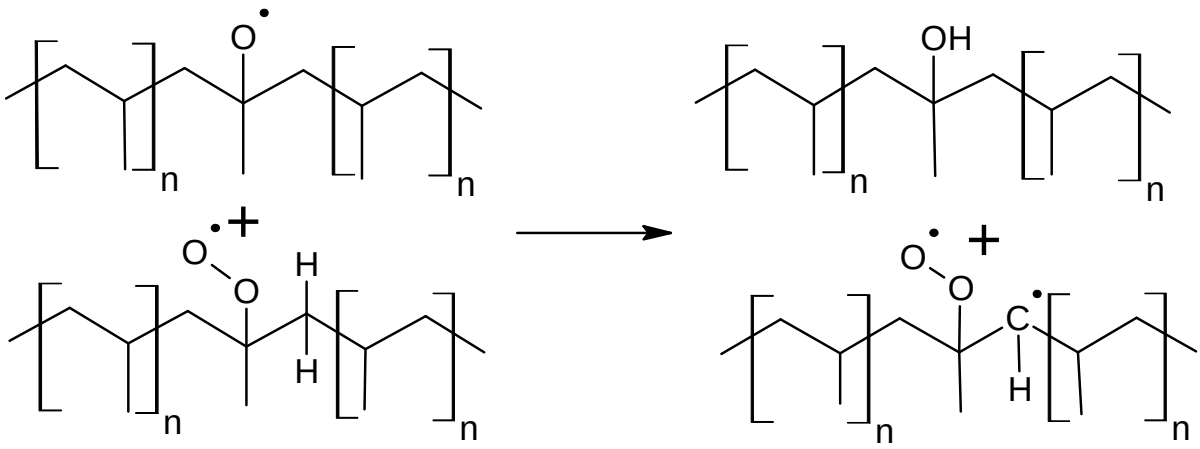


Figure 2.15: Secondary hydrogen elimination from an alkoxy radical.

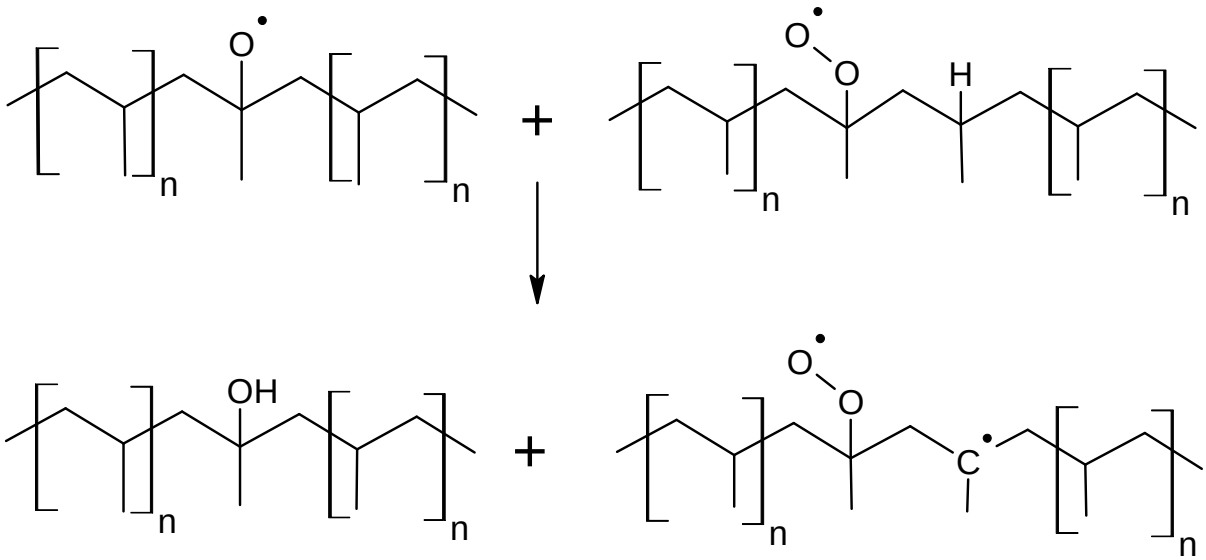


Figure 2.16: Tertiary hydrogen elimination from an alkoxy radical.

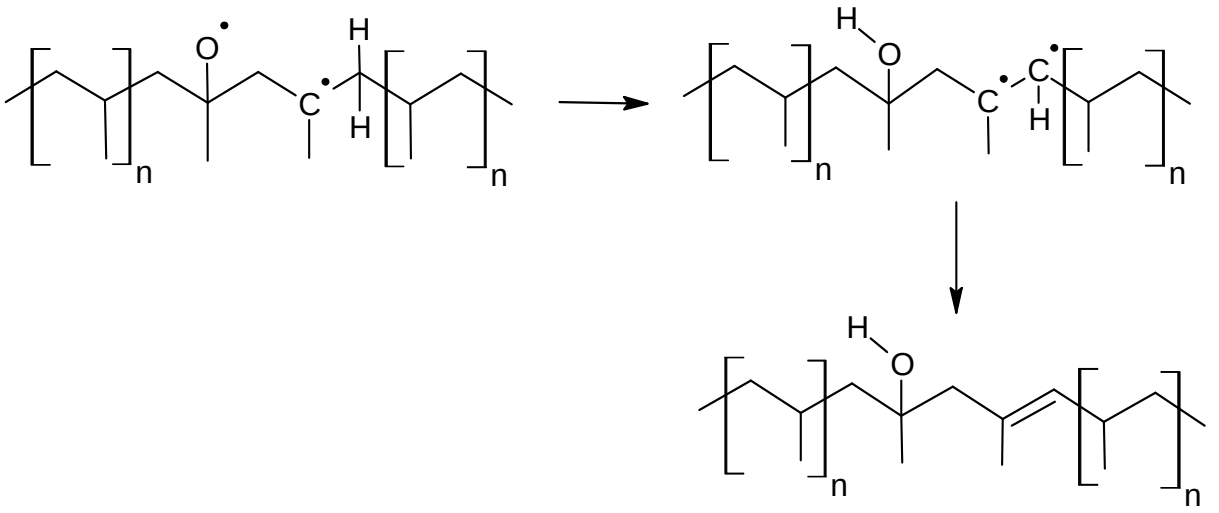


Figure 2.17: Intramolecular 1,5-hydrogen elimination and ‘‘ene’’ formation.

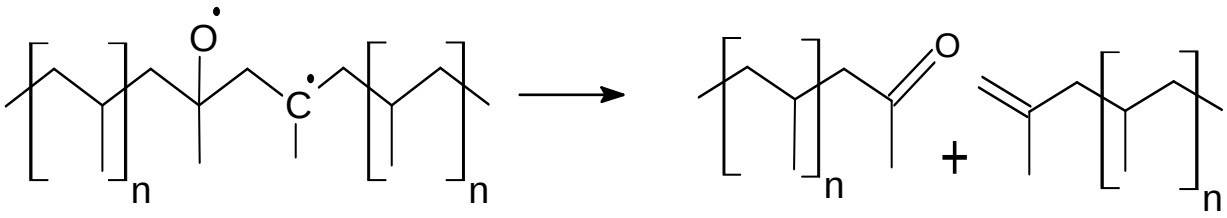


Figure 2.18: Decomposition of a tertiary alkoxy radical.

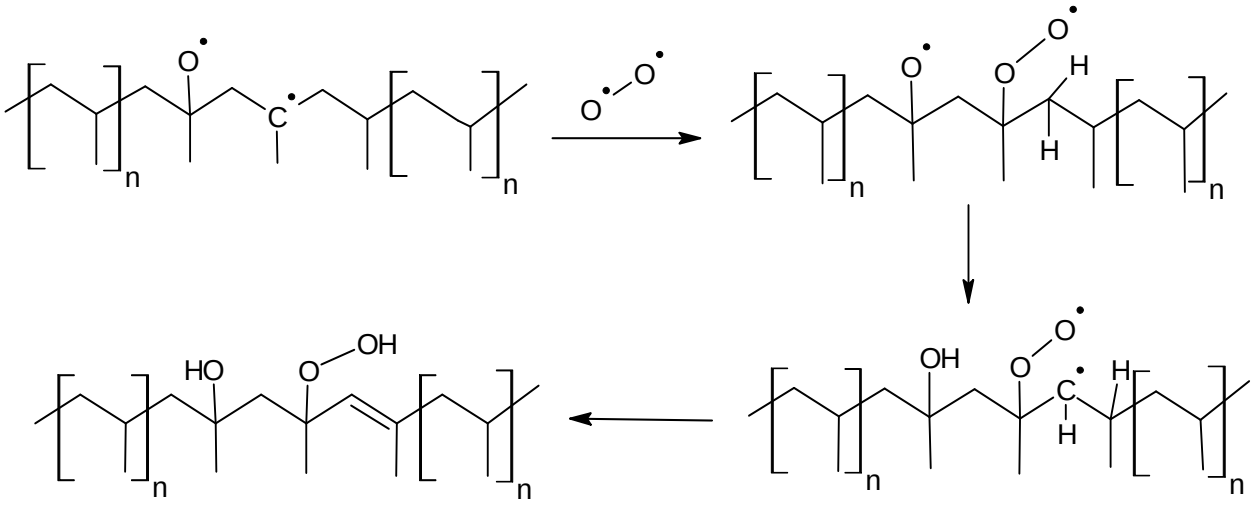


Figure 2.19: Peroxidation before hydrogen elimination and ‘‘ene’’ formation.

- **Peroxy Radicals**

Peroxy radicals formed during the propagation step lead to further hydrogen elimination. Usually this elimination tends to be intramolecular with adjacent tertiary hydrogen. Some studies have shown that peroxy radicals attack β position hydrogens, followed by those in the γ position. On the other hand, hydrogen atoms in the α and δ positions were not so prone to elimination. These reactions create vicinal hydroperoxides which are not stable, so the initiation rate is increased. Also if the peroxy radicals eliminate hydrogen intermolecularly the rate of the formed vicinal hydroperoxides is increased, because new radicals are created in another polymer chain.

When an alkoxy radical eliminates a secondary hydrogen with a peroxy radical formed adjacent to it, this leads to hydrogen elimination of the peroxy radical and a further ''ene'' formation because two alkyl radicals are formed [23, 24].

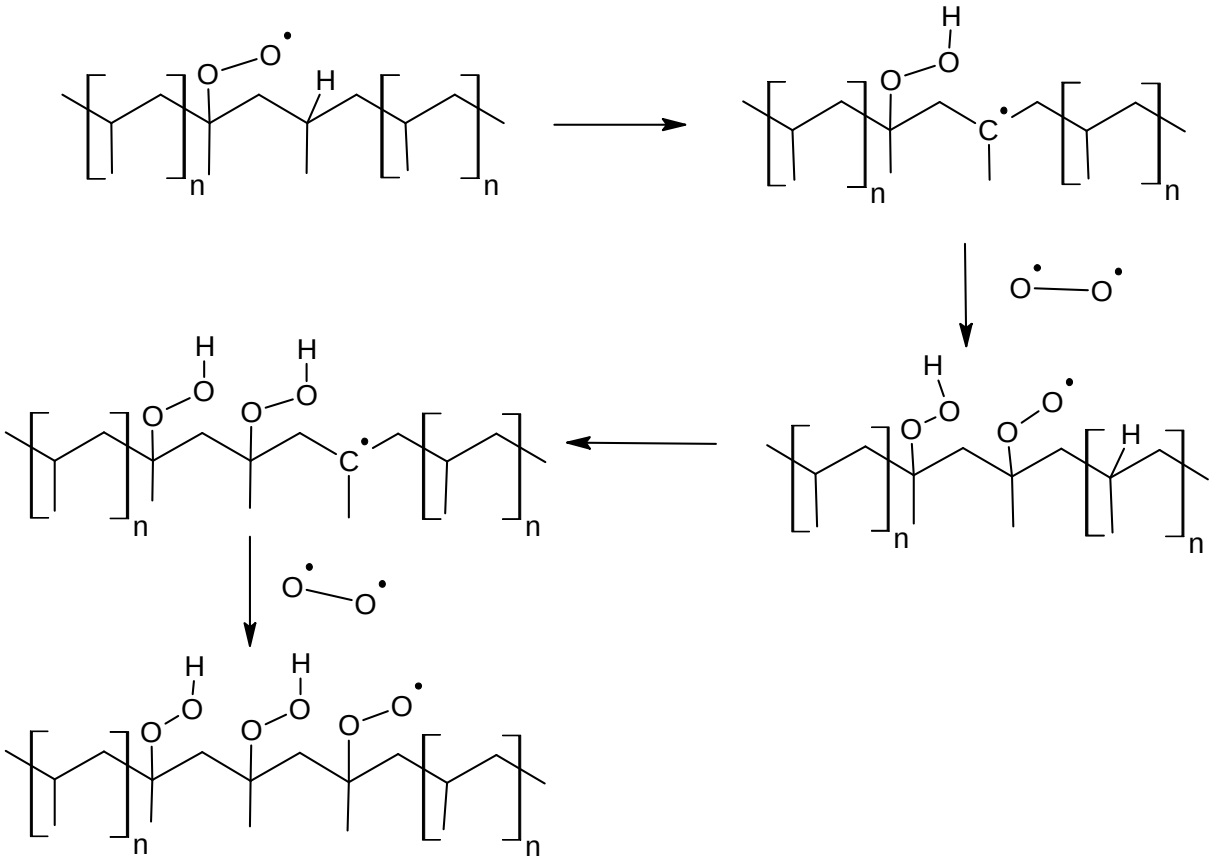


Figure 2.20: Formation of vicinal hydroperoxides.

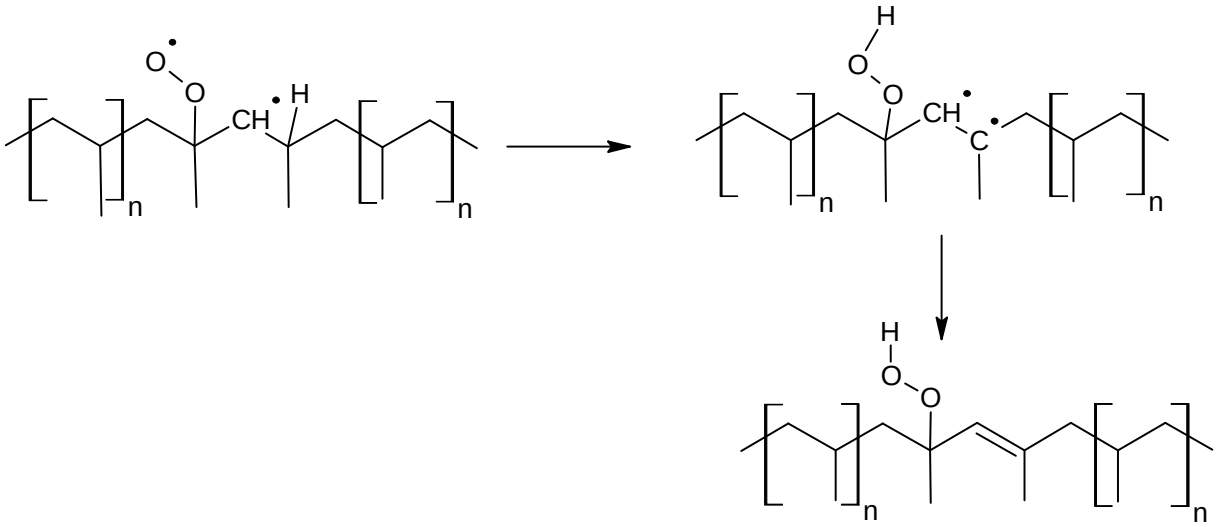


Figure 2.21: Hydrogen elimination of the peroxy radical and further ''ene'' formation.

Chain termination of peroxy radicals involves the reversible meeting of two such radicals, which forms a tetroxide. The breakdown of this tetroxide results primarily in the formation of alkoxy radicals and molecular oxygen [25]. The termination of the secondary tetroxides conforms to a cyclic decomposition pathway, during which a ketone and an alcohol are formed. These reactions take place at low temperatures while the other, with the formation of alkoxy radicals and molecular oxygen, occurs at temperatures above 100°C.

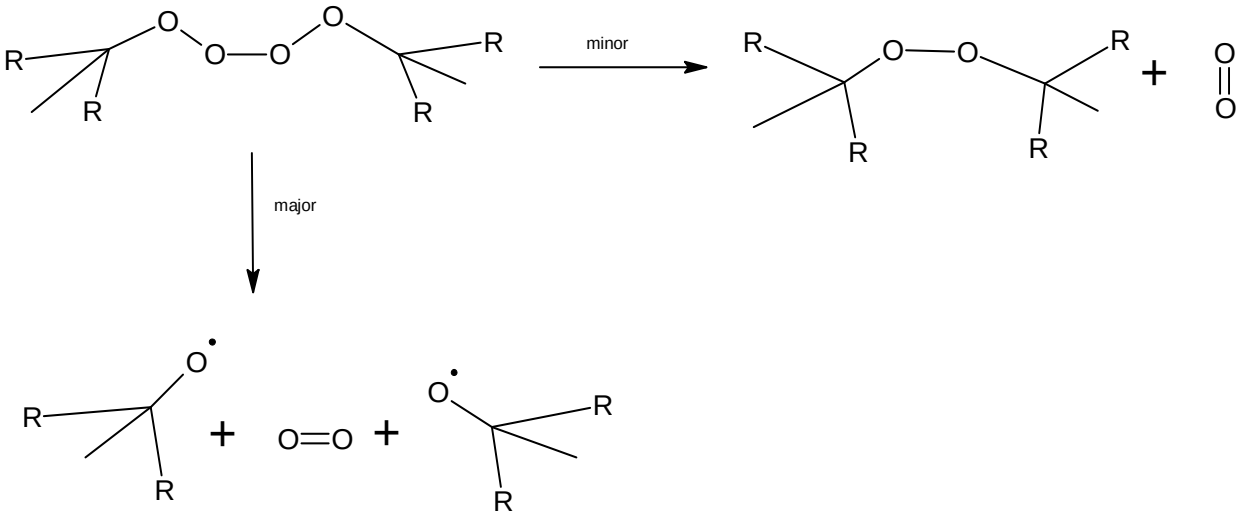


Figure 2.22: Thermal decomposition of the tetroxide.

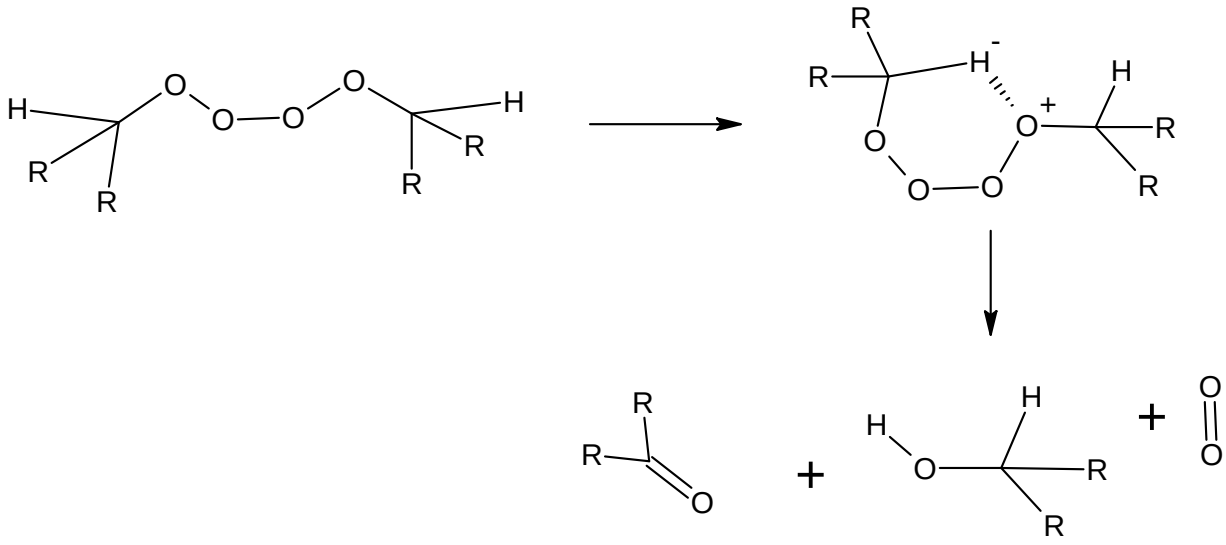


Figure 2.23: Low temperature breakdown of the tetroxide through a cyclic pathway.

Tetroxide formation is also achieved with intramolecular reactions. It must combine a secondary and a tertiary peroxy radical. The creation of hydroperoxide and peroxy radicals in polypropylenes chains is quite favoured, so it is likely to cause a reaction between the secondary and tertiary peroxy radicals. The reaction will decompose into aldehydes or ketones and molecular oxygen. Furthermore, the energy liberated in the reaction may result in chemiluminescence [23].

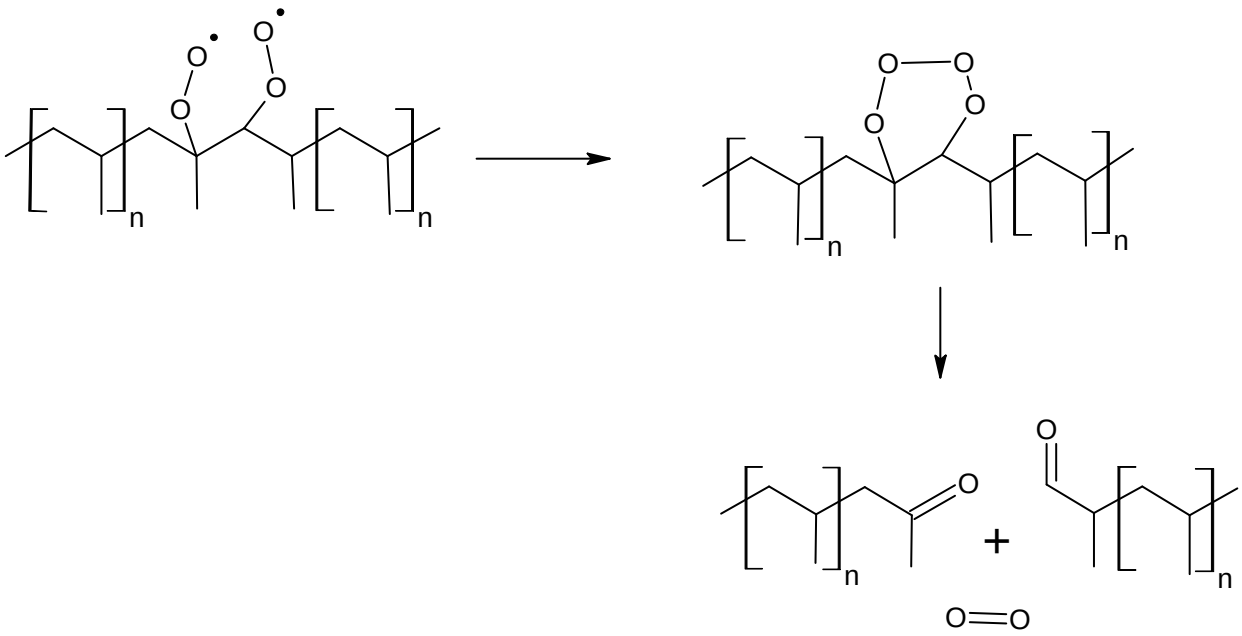


Figure 2.24: Adjacent peroxides forming a tetroxide and its further decomposition.

- **Hydroperoxides**

Thermal oxidation of polypropylene yields significant hydroperoxide concentrations. These products are formed from the hydrogen elimination of peroxy radicals and its concentration increases exponentially through the lifetime of the polymer. When these compounds are decomposed by thermal oxidation, the presence of metal ions or acids, the polymer deteriorates and loses its mechanical and physical properties. Some of the products formed during the self oxidation of hydroperoxides can be alkoxy radicals, hydroxyl radicals, peroxy radicals and even molecular water [24].

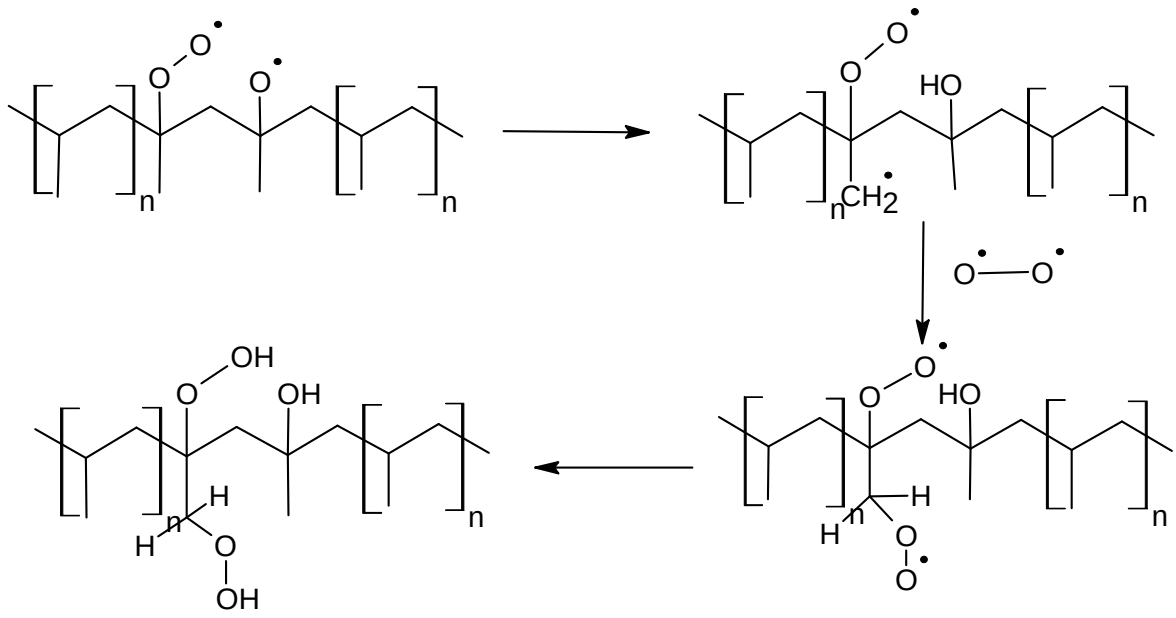


Figure 2.26: Formation of a primary hydroperoxide.

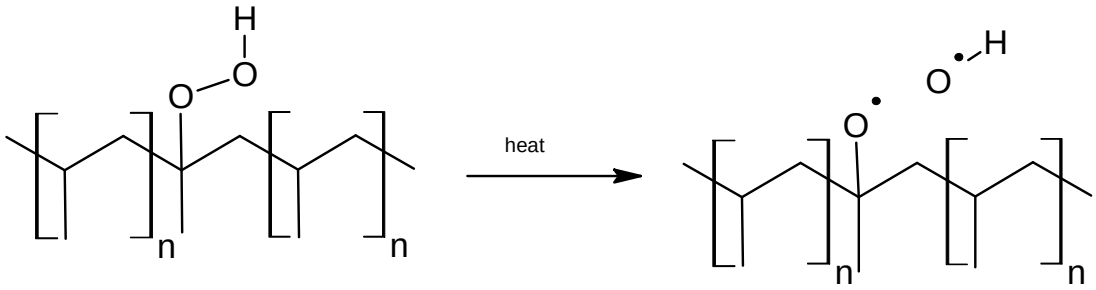


Figure 2.27: Breakdown of a hydroperoxyde.

During oxidation of the solid phase and in the melt, for polyethylene and polypropylene, as long as the temperature is not too high, hydroperoxides are accumulating. The formation of other species, such as aldehydes, is common too, and both species can be present at the same time. As a consequence there is a possibility of interaction between them [25 - 27]. It must be noted that the reaction of an aldehyde with a primary hydroperoxide is catalytic with respect to the aldehyde. As a matter of fact, the aldehyde transformed into acid in the reaction and is regenerated from the hydroperoxide. This reaction is of some interest in PP.

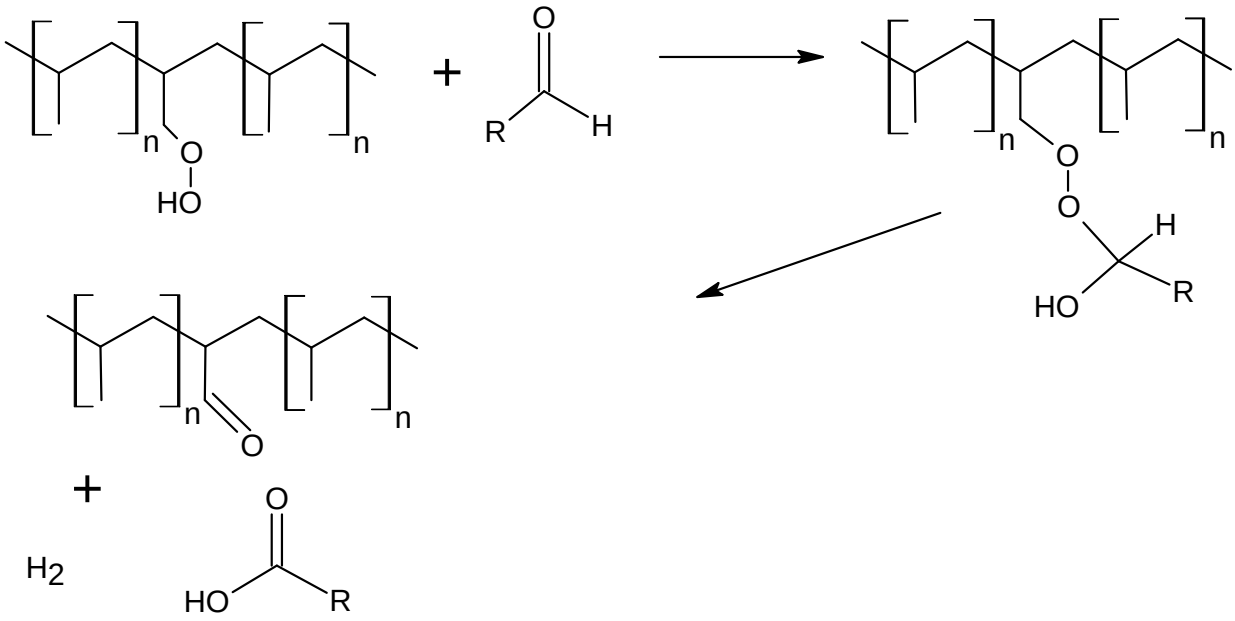


Figure 2.28: Reaction of aldehydes with primary hydroperoxides.

2.1.3.6. <u>Degradation Rate</u>

The degradation rate can be measured by the absorption of oxygen. Oxidation of polypropylene describes the kinetic curve of oxygen absorption, which has an S-shape. This curve is characterized by an induction period of self-acceleration and deceleration of oxidation in a deep stage of the process. The origin of kinetic chain occurs at hydroperoxide decomposition. The rate of this reaction (which is reaction of degenerate branching of kinetic chains) in the early stages process considerably exceeds the rate of primary initiation. This allows to neglect the primary initiation reaction and assume that the nucleation rate kinetic chain is the speed of degenerate branching.

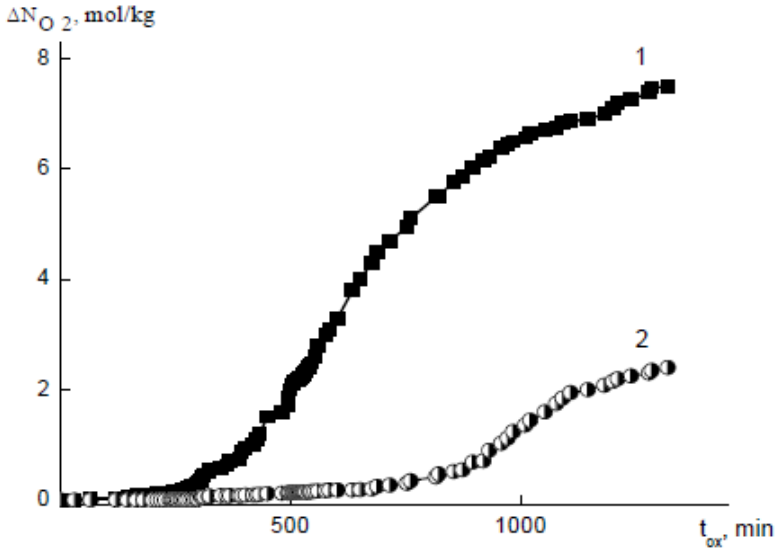


Figure 2.29: The kinetic curve of oxygen absorption of PP (1) in comparison with PE (2) [28].

2.1.3.7. Molecular Mass Changes

The exposure of polymer to high temperatures can develop a reaction which can change different aspects of the polymer, such as its molecular weight, and due to this change, its mechanical and physical properties. The reaction routes that cause the changes in the molecular mass and in the mechanical properties are cross-linking and chain-scission. The cross-linking of macroradicals in polyolefins cause an increase in the molecular weight of the polymer, whereas the random scission of polymer chains leads to a reduction of the molecular weight [29]. The way to measure the molecular mass changes is by measuring viscosity changes using the melt flow index (MFI). The most common polyolefins, polypropylene and polyethylene, show different behaviour during processing; polypropylene shows a increase of the MFI with time in the melt ar 200°C, which means that chain scission is the main reaction occurring and therefore the molecular mass is decreasing. However, polyethylene shows opposite behavior [17]. Cross-linking improves several physical and chemical properties in the polymers such as hardness, Young's modulus, heat resistance and solvent resistance. It also causes a molecular mass increase, brittleness and the elongation to decrease. This is contrary to

chain scission, which results in the reduction of the molecular mass and a decrease of the tensile strength [30].

2.1.3.8. Processing Degradation

Rotational moulding, injection moulding or other processing methods play an important role in a polymer's lifetime. During processing polymers are exposed to elevated temperatures (200°C to 250°C) and mechanical stress which, depending on the type of polymer, may subsequently cause dramatic changes in the polymer structure. During processing the polymer is melted and manipulated into the final product.

During processing the polymer is also exposed to oxygen, which attacks it due to the high prevailing temperatures. In the case of polypropylene, the oxygen initiates radicals R· from C-C and C-H bonds, as well as oxygen containing radicals such as RO· and ROO·, whose cleavage leads to the decrease in molecular weight reflected in the increase of the MFI [31]. In the absence of oxygen, instead of hydroperoxide formation, the polymer undergoes chain scission and depolymerisation.

2.1.3.9. Solid State Long Term Degradation

Polyolefins are used in many different applications where they are exposed to high temperatures. Without adequate stabilisation, the polymer will fail prematurely.

Oxidation processes in the molten state and solid state have many differences from each other. Polypropylene is a semi-crystalline polymer with a crystalline content between 30 and 70%. This depends on polymerisation conditions and on the sample characteristics. Oxidation in the solid state is initiated predominately in the amorphous domains of the surface of the polymer and then spreads to the surrounding amorphous parts throughout the polymer [32]. The oxidation

can spread slower or faster because of a number of factors that control it: oxygen pressure, temperature, initiation rate, sample thickness, supramolecular structure, etc. [33].

For the reasons mentioned above, it is important to study the polypropylene in solid state to understand the effects of long thermal degradation and which parameters can influence the polymer's life-time.

2.1.3.10. Diffusivity and Solubility of Gases

In polymer systems there can be three types of duffusion systems: gas-polymer, liquid-polymer and solid-polymer. Due to the fact that oxygen is one of the most important degradation initiators and volatiles compounds are also formed during the polymer oxidation, the diffusion system gas-polymer will be only analysed.

There is a model law of diffusivity and solubility created by Leonard and Jones which measures the activity of non condensable gases with pour molecular interaction such as: N_2, He, CO_2 and CH_4. This model law expresses that the diffusion of these gases is not dependant on time and concentration but it is on temperature and that the activation energy of diffusion is the most important factor to take into account. This energy is necessary for the gas molecule to jump into a new position ("hole"). It is thus obvious that larger the size of the diffusant molecule the higher the activation energy and lower the diffusion rate. Finally, it has to be considered that the diffusion only occurs in totally amorphous regions. In other words, crystalline regions are considered impermeable to the gas, so the higher the crystallinity degree the lower the diffusivity [1, 34]. During oxidation in processing, large amount of volatile compound are also released and these affect directly to the diffusion of oxygen. Compound such as, acetone, acetaldehyde and formaldehyde are diffused around the polymer matrix delaying or avoiding the oxygen diffusivity.

2.1.4. Crystallinity and Morphology

The crystalline and amorphous components influence a polymer in as much as the molecular weight of the polymer is influenced by the various fractions which make up the polymer. Actually, the crystallinity of a polymer is expressed in terms of that fraction of the sample which is crystalline. The definition of crystalline content is based on the premise that crystalline and non-crystalline parts can coexist. It is for this reason that X-ray diffraction patterns of most polymers contain both sharp and diffuse bands. Sharp bands correspond to crystalline regions while diffuse bands refer to amorphous regions [35].

Polypropylene, which is a semi-crystalline polymer, varies in degree of crystallinity and different types of crystal structures are possible depending on stereochemical structure, crystallisation conditions and the presence of additives. Properties of PP can be adjusted, depending on processing conditions and catalysts, by varying the crystallinity level of the polymer [7].

As previously mentioned in chapter 2.1.1, polypropylene has three different tactic forms which are different by their crystallinity degree. This chapter will analyse the crystallinty and morphology of the isotactic form as it is the one with more commercial interest because of its desirable physical, mechanical and thermal properties.

2.1.4.1. Isotactic Polypropylene

In all thermoplastics, properties are affected by the molar mass. When increasing the molar mass of the polymer chain, it is more difficult for the segments to arrange and fold in the correct way, so the crystallisation rate decreases.

In isotactic polypropylene it is naturally expected that crystal structure and crystallisation behaviours are not only dependent upon molecular weight and molecular weight distribution. Nucleation and cooling rate also affect the final morphological structure. Depending on the conditions, different forms can coexist and one polymorphic form can change in to another [7].

Isotatic PP can crystallise in four well known crystal structures or polymorphs: the monoclinic (α) form, the hexagonal (β) form, the triclinic (γ) form and the quenched form. Some reports

have also proposed the existence of a (δ) form. Among these crystal structures, the monoclinic (α) form is by far the most commonly encountered [36].

The morphology of the polypropylene crystals can be classified in three distinctly different levels. At the first level is the unit cell, discussed above (α, β, γ and δ forms). At the second level, there is the morphology at the lamellar scale and at the third level of morphology there is the spherulitic scale. Lamellas grow from a common origin, usually in spherical arrangements. Isotactic polypropylene exhibits a variety of spherulites classified by size, brightness and sign of birefringence [36]. The lamellar structure produces positive, negative and mixed birefringence. Negative birefringence results from spherulites in which radial lamella is predominant, while positive birefringence is due to spherulites with predominatly tangential lamellae. In mixed birefringence neither radial nor tangential spherulites are predominant. The birefringence changes from positive to negative as the crystallisation temperature increases and the tangential lamella undergo premelting [7].

Studies have shown that isotatic PP's prepared with a metallocene catalyst tend to form a mixture of alpha and gamma phases. This is because in chains of isotatic PP samples prepared with metallocene catalyst, the interchain defect composition and the intramolecular distribution of defects is random, whereas for isotatic PP obtained with a heterogeneous Ziegler-Natta catalysts, the mayority of the defects may be segregated in a small fraction of poorly crystallisable macromolecules, so fully isotatic sequences can be produced [37].

In the α-PP structure the isotactic polypropylene chain exhibits both left and right handed helical conformations. The α-PP structure consists of monoclinic unit cells. Crystallites grow to form sheet-like lamellae in a direction perpendicular to the principal axes of the helixes. Other lamellae can grow tangentially from the pre-existing lamellae, resulting in a crosshatched microstructure. The melting point (Tm) of α-PP is around 160°C.

The (β) crystalline form of isotactic PP differs from the alpha form by having a lower crystalline density and lower melting point. The beta form is metastable compared to the alpha form and will rearrange to the alpha structure when heated to approximately 100°C or placed under

strain. Otherwise, for β-PP the melting point (Tm) is 12-14°C lower than α-PP, so it is around 146-148°C [38].

The (γ) form of isotactic PP rarely forms under standard processing conditions. This form arises when an alpha crystalline material is sheared in the growth direction as crystals form. Gamma-crystallites form a crosshatched structure that is similar to the alpha-form, but in this structure crystallites grow in two directions simultaneously. Hence, the resulting structure is more uniform than that seen in alpha structure. The density of the γ-crystallites is higher than α and β crystallites [12, 39].

2.1.4.2 Effects of Crystallinity

Having a different degree of crystallinity affects directly many properties of the polymer, hence, it is necessary to analyse and understand how it influences subsequent stability. In the case of PP, which is a semicrystalline polymer, generally it has higher strength and more chemical resistance than totally amorphous polymers. On the other hand, amorphous polymers are more transparent and generally they have better ductility.

Firstly, it has to be mentioned that crystallinity directly affects the state transition as the melting point (Tm) and the glass transition (Tg). The melting point of a polymer varies with amount of crystallinity, a perfectly isotatic polypropylene has a theoretical Tm of 171°C while in a syndiotactic PP with 30% of crystallinity decreases to 130°C. The melting of polymer is marked by the onset of disorder, a higher degree of crystallinity involves a higher regularity in polymer structure and more energy to undo it and change the state. Anyway, the crystallinity is not the unique property that affects the Tm [7].

In semicrystalline polymers, the crystallites may be regarded as physical cross links that tend to reinforce or stiffen the structure. Viewed this way, it is easy to visualise that Tg will increase with the increasing of the degree of crystallinity [2].

Mechanical properties of PP are strongly dependent of its crystallinity as well. The increase of the crystallinity increases the stiffness, yield strength and flexural strength but decreases the toughness and impact strength. Spherulite size also affect to the mechanical properties. High

size spherulites, obtained at higher cyrstallisation temperatures, result in a more brittle behaviour of the PP while small size spherulites perform a more ductile one. However, in fatigue fracture tests, more damage is observed around broken region with smaller sizes wheras, less material damage is observed with higher size spherulites. At higher crystallisation temperatures the lamellar thickness also increases, tying the amorphous regions and making easier crack propagation along it [7].

2.2 POLYMER STABILISATION

Polypropylene has a high susceptibility to auto-oxidative degradation due to its tertiary hydrogens on the backbone structure, so it arguably never used without any stabilisation. Degradation could cause many changes such as colour change, brittleness and the loose of molecular mass of the backbone. Because of its high susceptibility to oxidation, which is due to its pendant methyl group and the methine hydrogen attached to the C-atom of the methyl group, unstable PP can start to decompose immediately after formation. To protect olefins from oxidative degradations and environmental changes, antioxidants are added to the polymer because they are capable to moderate the rate of oxidation by absorbing the heat or the light radiation energies. Antioxidants are chemicals included in the polymer resin before or after processing in order prevent from a particular deterioration. Many engineering or industrials applications require the additions of more than one additive or antioxidant [7, 40].

Nowadays there is a wide variety of additives which are added to thermoplastic resin systems to enhance or obtain specific desired properties. Once an additive has been selected, however, other factors must also be considered. The method of preparation, or the impurity level for example, are both important. Processing conditions are also an important criterion. Some additives are impaired by exposure to the high processing temperatures of engineering thermoplastics. Others may be added to the compound specifically to protect it against such high temperatures. Otherwise, if the main issue is the exposure to ultraviolet light or a bacteriological attack, different additives may be used. In some cases they are used for

contradictory purposes: to improve electrical insulation, for example, or to destroy it and make the compound conductive. The chemistry of additives is often extremely complex and the choice of materials can be bewildering to anyone but a specialist. Nevertheless, it useful for designers, engineers and processors to have some overall familiarity with additives and their technology [41].

Antioxidants are necessary components for all PP compounds and the selection of such ingredients is an important factor in determining the success of a given commercial material. For optimum processing stability a single antioxidant of the phenol-alkane type tends to give the best results. However, for long term service stability at high temperatures it is more common to employ a synergistic mixture. Prolonged oven heating leads to embrittlement and embritllement time is useful to measure the efficiency of the antioxidant. Small amounts of antioxidants are usually required; 0.05-0.25 % of antioxidant by weight of polymer is often enough to obtain an appropriate result, although for some applications the antioxidant level may exceed to 0.8% [42].

It is important to remark that the thermal stabilisation of PP for service is very different than thermal stabilisation for processing. In the former case, the temperature usually does not exceed more than 120 °C, but the polymers are exposed for a much longer time. On the other hand, processing temperatures are between 200-250°C, i.e. 100°C higher than service temperatures. It is important to choose the correct antioxidant depending on the application [6].

2.2.1. Primary Antioxidants

In order to retard the oxidation it is necessary to intercept free radicals responsible for chain propagation. Chain breakers or scavenging antioxidants are usually referred to as primary antioxidants [43].

Hindered phenols and aromatic amines make up the majority of primary antioxidants. These primary antioxidants donate their reactive hydrogen to remove chain propagating radicals from the PP matrix. To sufficiently terminate the oxidation process, the antioxidant radical must be rendered stable to prevent the continuation of propagation of new radicals. These radicals, in most cases, are stabilised via electron delocalisation or resonance [44].

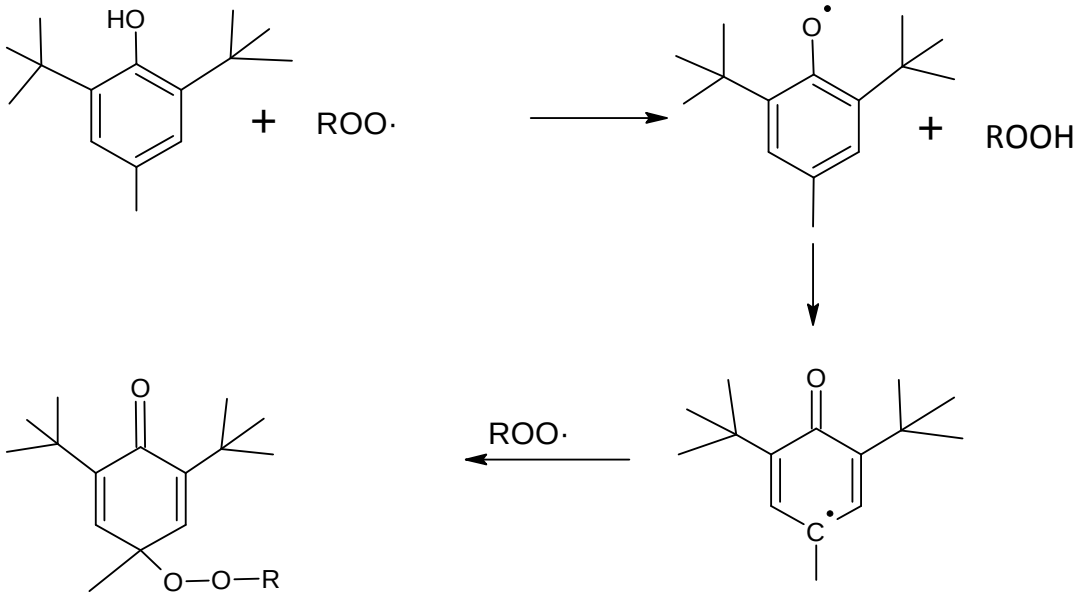


Figure 2.29: The chain terminating mechanism of BHT, a hindered phenolic compound.

2.2.1.1. <u>Hindered Phenols</u>

Hindered phenolic compounds are the preferred type of primary antioxidants for thermoplastics. Included in this category are simple phenolics, bis-phenolics, polyphenolics and thiobisphenolics.

The most familiar hindered phenol is 2,6-di-t-butyl-4-methylphenol, also known as butylated hydroxytoluene or BHT. BHT has been the workhorse antioxidant for polyolefins, styrenics, vinyls and elastomers. Although BHT is a very effective chain terminator, it suffers from a major drawback, namely its high volatility. The replacement of the methyl in the para position by long aliphatic groups has succeeded in reducing the volatility. Bisphenolics and polyphenolics

provide dual benefits of high molecular weight, hence lower volatility, with comparatively low equivalent weights [44].

Stabilisation is achieved in BHT due to electron delocalisation inside the aromatic ring. The antioxidant behaves like a chain breaking donor because of the donation of a hydrogen by the reactive OH group, which removes a chain propagating radical from the system. The reactive peroxy radical is turned into a much less reactive phenoxy radical and hydroperoxide. The donation prevents the loss of a tertiary hydrogen atom from the PP backbone, so the propagation of the auto-oxidation is suspended or delayed [45].

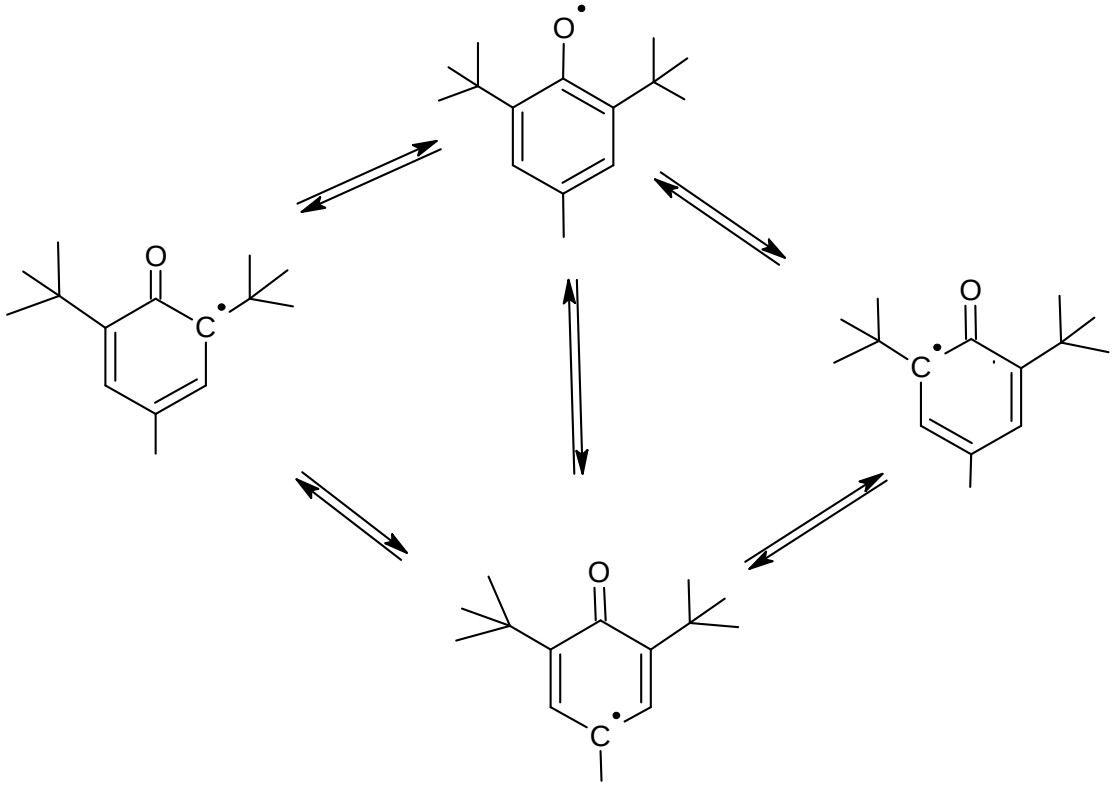
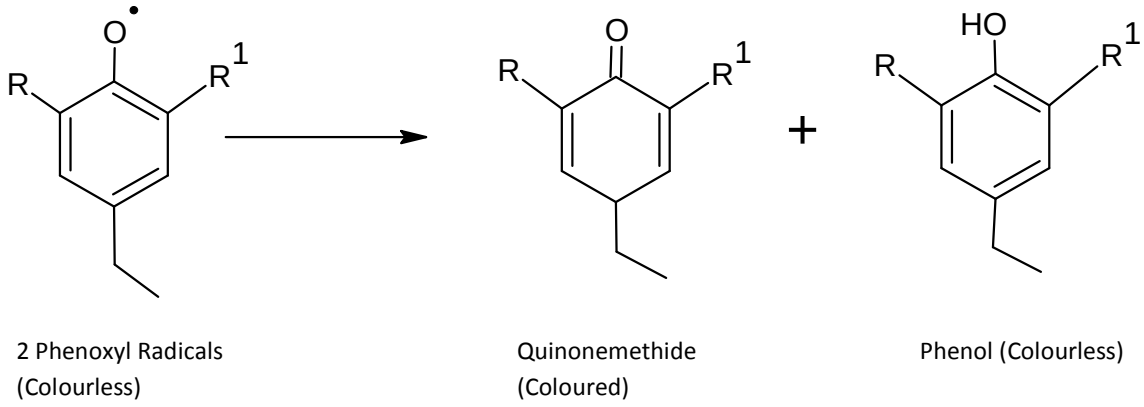


Figure 2.30: Phenoxy radical stabilisation through electrodelocalisation.

Although hindered phenols have been shown to be very long term stabilisers, some degradation occur when high temperatures are involved [46]. For high temperature applications such as bonnet automotive components or Rotational Moulding, antioxidants with higher molecular mass are required. For this, polyphenolics are the most reliable compounds.

However, the use of these of these compounds is more expensive. The most prominent of the polyphenolics is tetrakis [methylene-(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane, which has the tradename Irganox 1010 (Ciba) or Songanox 1010 (Songwon Industries).

BHT is not very reactive at lower temperatures, but it could become a chain propagator at high temperatures [47]. For example, if BHT as a phenoxy radical carries out a second primary antioxidant reaction, this can lead to a new chain reaction in their decomposition. Such reactions include the formation of quinonoid transformation products during further oxidation. These products give some degree of colour to the polymer, but they show a high contribution to the overall long term stability [48].



2 Phenoxyl Radicals (Colourless)

Quinonemethide (Coloured)

Phenol (Colourless)

Figure 2.31: Formation of coloured quinonoid products through disproportionation.

Other problems involved with the use of stabilisers are migration, volatilisation and staining. To overcome these issues, antioxidants which have high molecular masses, such as polyphenolics or bisphenolics, are employed. In the melt state the physical iteractions between antioxidants the polymer, such as volatibility and solubility play an important roleI. Despite is the phenolic OH being an active moiety in antioxidants which is involved in the chemistry of stabilisation there is also a second structure of the antioxidants responsible for the physical behaviour of the molecule in the polymer. Under certain conditions the secondary structure may impact the behaviour of stabilizer to such an extent that its chemical effect is completely overridden and stabiliser loses its ability to stabilise [40]. The second moiety or the moiety of the para

substituent plays an important role in the activity of the hindered phenolic antioxidants. The reactivity of the OH group is directly affected by the electron accepting-donating properties of the para substituent. Electron donating groups increase antioxidant activity, while electron accepting groups decrease its activity.

2.2.1.2. Aromatic Amines

Aromatic amines are chain breaking donors and excellent H-donors. The hydrogen atom is donated from the reactive NH group which removes a chain propagating radical from the polymer matrix. Aromatic amines are superior to phenolics for high temperature applications such as underhood automotive applications, but they are not used for food-packing applications. This could be due to their easy decolourisation and their applications are limited if they are used with pigments such as carbon black [7, 49].

2.2.2. Secondary Antioxidants

Secondary antioxidants, or peroxide decomposers, inhibit PP oxidation by decomposing hydroperoxides. These products are reduced to more stable alcohol species by an oxidation-reduction reaction. The most common secondary antioxidants are phosphites and thioethers; both are oxidized to phosphates or sulphates respectively.

Secondary antioxidants are often combined with primary antioxidants in order to obtain better results than with each one alone. By combining different amounts of additives, better synergism can be obtained. Unlike primary antioxidants, secondary types are generally inadequate to be used alone. Also, the yellowness of the polymer can vary depending on the quantity of the secondary antioxidant [2, 7].

2.2.2.1 Phosphites

Antioxidants based on phosphorous such as phosphites and phosphonites are well known to be effective as polymer stabilisers, especially during processing. They belong to the family of secondary antioxidants and as it has been explained above, are often used with primary

antioxidants to be more specific with phenolics due to their high synergism. The phosphites tend to reduce the development of yellowness of the polymeric matrix generated from the phenolics [51] when it is exposed to heat, UV light or gamma rays, but they are sensitive to moisture and this could become problematic in some instances [50].

Just as phenolic antioxidants, phosphites increase the induction time to oxidation proportionally to their concentration. During stabilisation particular attention is paid to the reactions. The phosphites reduce the hydroperoxides to alcohols at the time as they are oxidized to phosphates. During this reaction the non-bonding electron pair directly interact with an oxygen atom from the hydroperoxide molecule and this leads to an assisted hydrogen transfer. These reactions are often quite fast, but the R groups of the phosphite could retard it. Usually it is a stoichoimetric reaction in a 1:1 ratio. Phosphites can also undergo other types of reactions which are undesirable. One of these is the hydrolysis of the phophite to generate a derivative phenol, usually with a low molar mass. During the reaction phosphites are oxidized to phosphorous acids and they can corrode processing equipment, form coloured spots and other undesiderable properties [51].

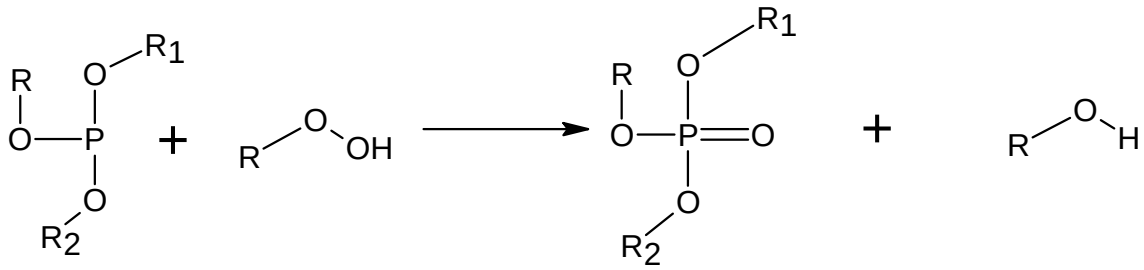


Figure 2.32: Reaction between phosphites and hydroperoxides.

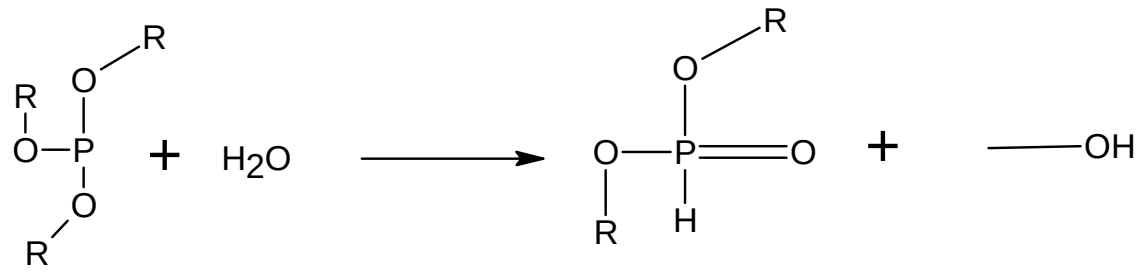


Figure 2.33: Hydrolysis of phosphites.

Phosphites also could undergo reaction with other products such as alkoxy and alkylperoxy radicals. The effectiveness of these reactions depend on the nature of the R' substituent of the phosphate. In some cases, the R'O· radical created during the reaction is stable enough and it is incapable to propagate the chain breaking mechanism. When other radicals are formed, e.g. R· or RO·, the propagation step proceeds. It has been found that hindered phenol phosphites tend to form R'O· radicals, while aliphatic ones preferably tend to form R·. Both can form RO· type radicals [52].

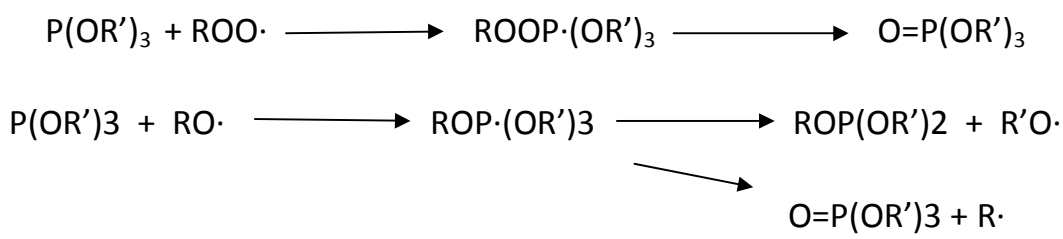


Figure 2.34: Phosphite reactions with alkoxy and alkylperoxy radicals.

2.2.2.2. Thioethers

The majority of the thioethers are esters of thiopropionic acid with fatty alcohols which have lots of similarities with the phosphites, but their behaviour is a bit more complex [53]. Both secondary antioxidants have the same ability to decompose hydroperoxides, but thioether can decompose up to several moles [54]. The reaction between thioethers and hydroperoxides yields sulphoxides and alcohols. The further oxidation of the sulphoxides form acidic catalysts that are even more powerful hydroperoxide decomposers than the original thioethers.

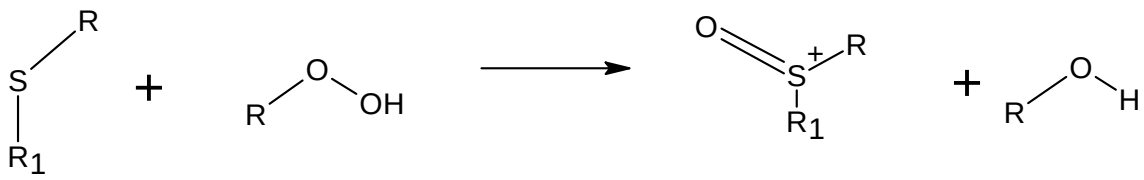


Figure 2.35: Reaction of thioethers and hydroperoxides to yield sulphoxides and alcohols.

Thioethers are very good synergistic companions for primary antioxidants. This combination translates into a significant cost savings by replacing a portion of higher priced phenolic antioxidants with the relative less expensive thioether. Their main drawback is the odor they can impart to the polymer, which restricts their use in food packing applications [44].

Thioether in reaction with hydroperoxides form various sulphurous acids, which can also form different sulphurous esters. Esters of sulphurous acid are supposed to show antioxidative effects, comparable with phosphites, due to an analogous electronic structure. As sulphurous acid derivates are known to be a relatively rapid oxidative compound, they should be oxidised by hydroperoxides. These esters react more slowly in comparison with trivalent phosphorous compounds, but they are able to decompose hydroperoxide catalytically. Beside these sulphuric acid esters SO_2, SO_3, and H_2SO_4 also take part as catalysts in the reaction [55].

2.2.3 Hindered Amine Light Stabilisers

Hindered phenols have been shown to be very effective long-term stabilisers, but they can lead to a discolouration of the polymer. Because of this, hindered amine light stabilisers (HALS) have gained attention as heat stabilisers for polyolefins. They are effective as heat antioxidants at low and moderate temperatures between 30°C and 80°C. At higher temperatures between 100°C and 150°C, the behaviour of the phenolic antioxidants and HALS is quite different. The phenolic antioxidants have a dramatic degradation after the induction period, while HALS display a degradation which depends on the concentration, so the mechanical properties degrade in a more gradual way. This is related to the different modes of action of the stabilisers and how HALS cannot prevent a certain amount of degradation.

The effectiveness of HAS is attributed to the presence of nitroxyl radicals (NO·). The HALS is oxidised by peroxy or hydroperoxides in a relatively slow and temperature dependant reaction. The nitroxyl radical is able to scavenge radicals which are formed during oxidation [56].

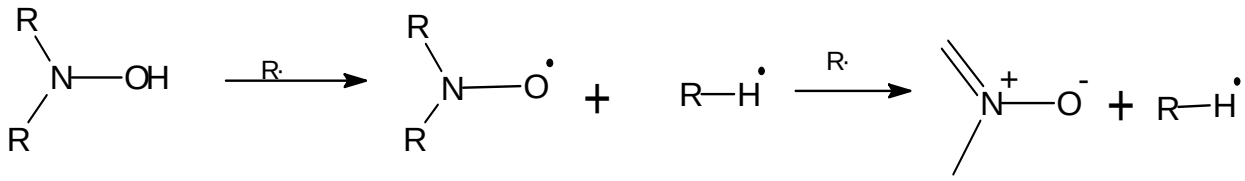


Figure 2.36: Removal of free radicals.

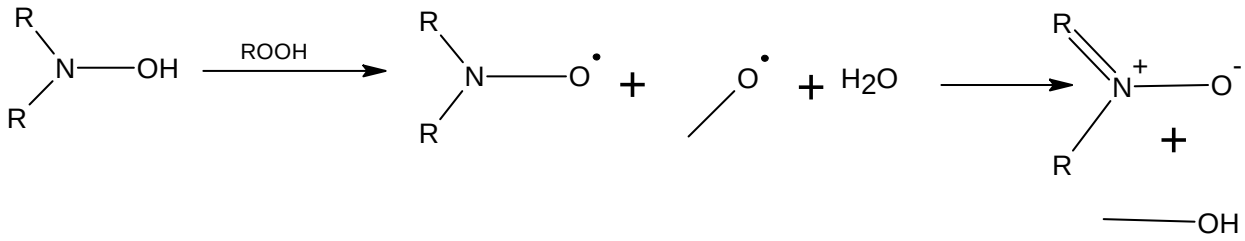


Figure 2.37: Decomposition of hydroperoxides.

2.2.4 Controlled Release of Polymer Stabilisers

It has been recognised for several decades that the migration of stabiliser molecules in a polymer matrix can make significant changes to its properties. Strong stabilisation activity often goes hand in hand with high mobility as the stabiliser should ideally be able to diffuse rapidly to the oxidation sites. However, due to their mobility these stabilisers can leave the polymer without being active by evaporation or leaching or by the early oxidation of the antioxidant. The physical state of the polymer has an influence in the mobility and solubility of the antioxidants and the oxygen as well. Therefore, the majority of industrial antioxidants and stabilisers are arguably far from ideal. So, from the 80's onwards, significant research has been focussed on physical loss of additives from polymers [57 - 62].

The polymer industry is not alone in investigating controlled release technologies. The agricultural and pharmaceutical industries are also exploring controlled release technologies for moderating the release of drugs and fertilisers/pesticides, respectively. In recent years the

paint industry has also started to examine controlled release methods for fungicides and other antimicrobials [63 - 66].

In general, silicates and zeolites are some of the most utilized compounds for encapsulation and controlled release. Silica is particularly attractive, due to its characteristics, such as particle size, porous structure and surface morphology and surface chemistry which can feature a variety of different silanol groups, which can interact with the molecule whose release is to be controlled. The pore size and active groups on the surface determine how strongly an additive will be adsorbed. The antioxidants and stabilisers may be chemisorbed or physisorbed on the silica surface, thereby restricting their mobility. The antioxidants will therefore keep on inhibiting degradation reactions. Although these types of processes will control and influence the performance and the end use properties of polymers, examination of the literature reveals that little attention has been paid to this area of additive chemistry [67, 68].

During this project, gel silica was investigated as a controlled release substrate.

2.2.4.1 Silica Gels

Silica is an indispensible part of both the natural and technological worlds. Moreover, silica is one of the most extensively used inorganic fillers with applications like antiblocking or reinforcing the polymer matrix. The compound silica (SiO_2) is formed from silicon and oxygen atoms, because these atoms are the most abundant on the Earth's surface. Three different crystalline structures can be formed from silica: quartz, tridymite and cristobalite. The most common one is quartz and when it is analysed by X-ray diffraction its atomic structure can be deduced. Four oxygen atoms linked together to form a tetrahedron. In the centre of this structure there is a silicon atom. Therefore, the structure is called a silicon-oxygen (SiO_4) tetrahedron. When these tetrahedrons are linked together by sharing an oxygen atom from a corner, quartz is formed. Otherwise, silica can be also found in its amorphous state.

When silica forms bonds with other inorganic elements such as potassium, calcium, magnesium or iron, silicates are formed. On the other hand, when silica bonds with organic elements (carbon), silicones are formed. Silicones are often polymeric [69].

Over the decades, alo of research has explored the surface properties of silica gel. Silica surfaces are usually covered with a layer of hydroxyl groups and it has several consequences. First, it adsorbs H_2O which can be largely removed by drying at high temperatures reaching 600°C or with suitable reagents, but in general it is very difficult to dry a silica surface completely. Wide variations exist in silica gel surfaces depending on the concentration of hydroxyl groups. The difference in the concentration may reflect in different degrees of regularity and crystallinity [68]. Because of these hydroxyl groups hydrogen bonds are created which make interparticle interactions very strong. Moreover, hydrogen from hydroxyl groups can be substituted to give Si-O-M. In this case, M can be any catalytically active metal as V, W, Mo, Cr. This makes silica an excellent material for catalysis [71].

The siloxane group Si-O-Si is non-polar and it provides a hydrophobic character to a silica surface. However, as mentioned before, there are many hydroxyl groups that are strongly hydrophilic. These different hydroxyl groups are typical on the surface and they can be identified by FTIR. The groups are the following: Isolated silanols, silanediols and silanetriols. Vicinal silanols can also be develop by hydrogen bonding and through water elimination a siloxane is formed. Because isolated silanols are more reactive than vicinal silanols, they promote hydrogen bonding between particles. Generally, the average surface density of silanol groups is around 3-6 silanol/nm^2 [72].

3. ANALYTICAL PROCEDURES AND PROCESSING TECHNIQUES

The methods of processing and analysis will be described in this chapter.

3.1 ANALYTICAL PROCEDURES

3.1.1 Fourier Transform Infrared Spectroscopy

Infrared spectroscopy is a technique based on the vibration of the atoms of a molecule. In transmission Fourier transform infrared spectroscopy (FTIR), a beam of infrared light passes through the sample typically compressed in a KBr disc or like a film. Then, the Fourier transform mathematical operation is applied to obtain a spectrum which can be displayed. The spectrum displays which fraction of the incident radiation is absorbed at a particular wavelength. The energy at which any peak in absorption spectrum appears corresponds to a frequency of a vibration of a part of the sample molecule.

The vibration of the molecules can involve either a change in bond length (stretching) or bond angle (bending). Some bonds can stretch in-phase (symmetrical-stretching) or out-of- phase (asymmetrical-stretching). If the molecule has different terminal atoms, stretching is no longer a symmetrical or asymmetrical vibration of similar bonds, they will have different proportions of vibration depending on the type of group. For a vibration to give rise to the absorption of infrared radiation, it must cause a change in the dipole moment of the molecule. The larger this change, the more intense the absorption band will be. Because of the electronegativity difference between carbon and oxygen, the carbonyl bond will always be polarized and thus gives rise to the characteristically intense carbonyl peaks.

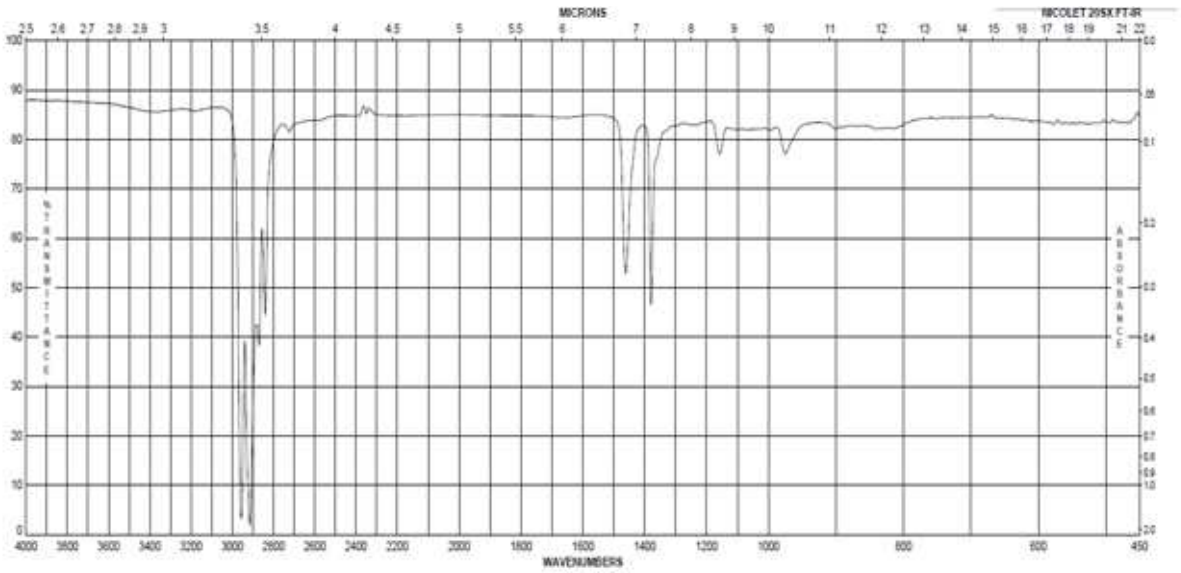


Figure 3.1: Illustration of typical FTIR for iPP [73].

The ranges of collecting data for FTIR go from wavenumber 400 to 4000 cm^{-1}. FTIR is not only an instrument for chemical structure determination, it can be used for quantitative analysis also. The intensity of each peak in the absorbance spectrum is directly proportional to the concentration of the particular chemical group.

In the case of PP, the atactic and the isotactic forms are overlapped due to the crystalline structure. The region from 1200-800 cm^{-1} is where peaks related to the tactic structure appear, also called fingerprint region [73]. With the isotactic bands and the crystalline phase band, the crystallinity content of the polymer can be measured, however, DSC and XRD methods are much more accurate for this measurement.

Table 3.1: FTIR absorption bands of isotactic polypropylene [73].

Wavenumber (cm^{-1})	**Assigned Band**
2958	*v (stretching) CH_3*
2885	*v (stretching) CH_3*
2838	*v (stretching) as CH_2*
1461	*δ (symmetrical bending vibration) CH_2*
1380	*δ (symmetrical bending vibration) CH_3*
1165	*Isotactic Band*
997	*Isotactic Band*
977	*Isotactic Band*
841	*Crystalline Phase Band*

One of the best advances of FTIR in polymer degradation studies is that thin films can be studied, thus reducing the sample required for the analysis [74, 75].

Table 3.1: FTIR absorption bands in degraded polypropylene [6]

Wavenumber (cm^{-1})	**Chemical Group**
3270-3350	*Aliphatic hydroperoxide*
3190-3200	*Aromatic hydroperoxide*
1720 and 1705	*Carboxylic acid*
3409	*Hydroxyl group from carboxylic acid*
1757	*Carboxylic acid monomeric form / anhydride strech*
1739	*Aliphatic ester*
1731	*Benzoic acid*
1725	*Aldehyde*
1715	*Saturated aliphatic ketone*
1702	*α and β unsaturated ketones*
1685	*Aromatic ketone*

3.1.2. Attenuated Total Reflectance Infrared Spectroscopy

Infrared reflectance spectroscopy has found application when the samples are difficult to manipulate, such as polymers, food and rubbers. Reflectance spectra in the mid-infrared region are not identical to the spectrum obtained by absorption, but in general they are quite similar and they provide the same information. Reflectance spectra can be utilized for quantitative and qualitative analysis. Reflectance methods can be divided into two categories. Internal

reflectance measurements can be made using an attenuated total reflectance (ATR) cell in contact with the sample. There is also a variety of external reflectance measurements which involve an infrared beam reflected directly from the surface.

Attenuated total reflectance, unlike other forms of infrared analysis, has the advantage that the sample needs little or no preparation, which makes the analysis quicker. It does not matter in which state the sample is, solids and liquids can all be analysed.

Attenuated total reflectance spectroscopy utilizes the phenomenon of total internal reflection. A beam of radiation entering a crystal will undergo total reflection when the angle of incidence is bigger than the critical angle. Theoretically and experimentally it is proved that the beam penetrates a certain depth into the sample. The depth can vary from a fraction of a wavelength to some wavelengths, depending on the reflectance indices of the internal reflection element and the sample and the IR wavelength [76]. This never exceeds the micron-scale, so the analysis is relatively surface specific, but by no means as surface specific as X-ray photo-electron spectroscopy which has a penetration depth in nanometre range. Degradation in polymers appears more likely on the surface of the samples.

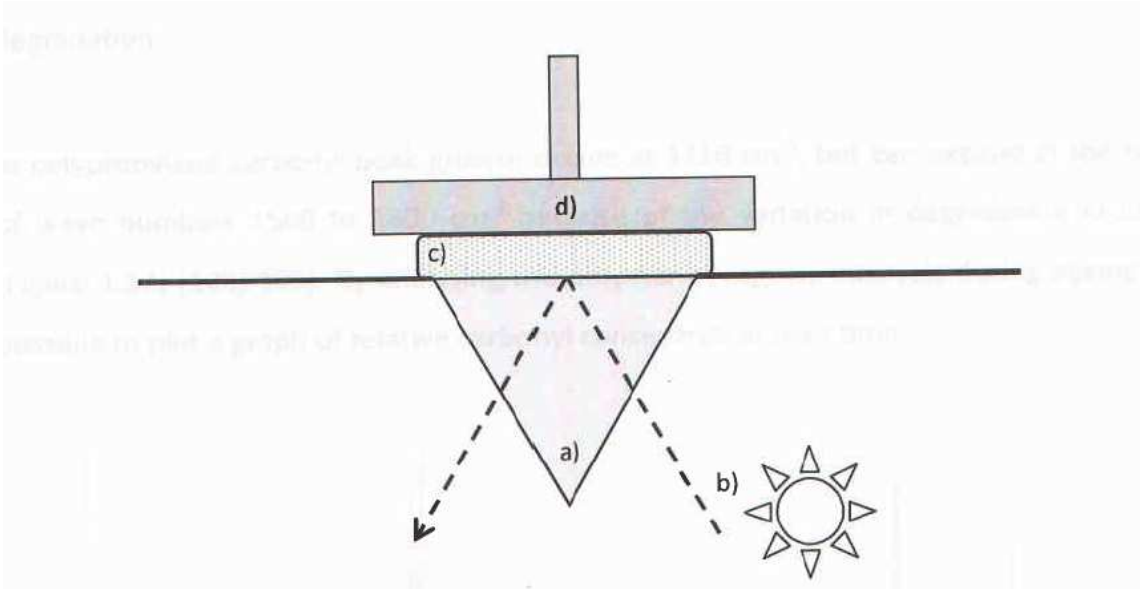


Figure 3.2: Diagram of the attenuated total reflectance spectromer. a) Diamond prism b) Light source c) Sample d) Applied pressure [76].

The crystals used in ATR cells are made from materials that have low solubility in water and have a very high refractive index. Such materials include ZnSe, Ge, thallium-iodide (KRS-5) and diamond.

3.1.3. FTIR and ATR for Carbonyl Peak Induction

Carbonyl formation is the result of the oxidation of the polymer matrix and it can be analysed by infrared spectroscopy. When the concentration of antioxidant is relatively high, the carbonyl concentration tends to be low. However, at the time when the concentration of antioxidants starts to go down, the carbonyl concentration starts to rise. Usually, one must wait until all the stabilisers are consumed to see an increase in the carbonyl peak.

As can be seen above, carbonyl peaks tend to appear around 1710 cm^{-1}, but these may occur from 1800 cm^{-1} to 1500 cm^{-1} because of the variation of the degradation products. The analysis of the polymer at regular intervals while simulating the rotomoulding process can provide information on the increase of carbonyl peak concentrations over the processing time [77].

To determine the carbonyl concentration of the polymer, it is necessary to choose an internal standard band in the polymer spectrum. The internal standards are peaks that remain unchanged during the degradation of the polymer. There are many peaks that can be useful as reference for polypropylene: 840, 1166, 1455, 2720 and 2780 to 3000 cm^{-1}. Some of them are very sensitive to the crystallinity of the PP and others overlap with several other peaks, which make the ones occurring at 2720 and 2780-3000 cm^{-1} the best peaks to take as internal standard. The absorption of these peaks is associated to CH_2 symmetrical and asymmetrical stretching and to CH_3 symmetrical and asymmetrical stretching as well as CH bending [78].

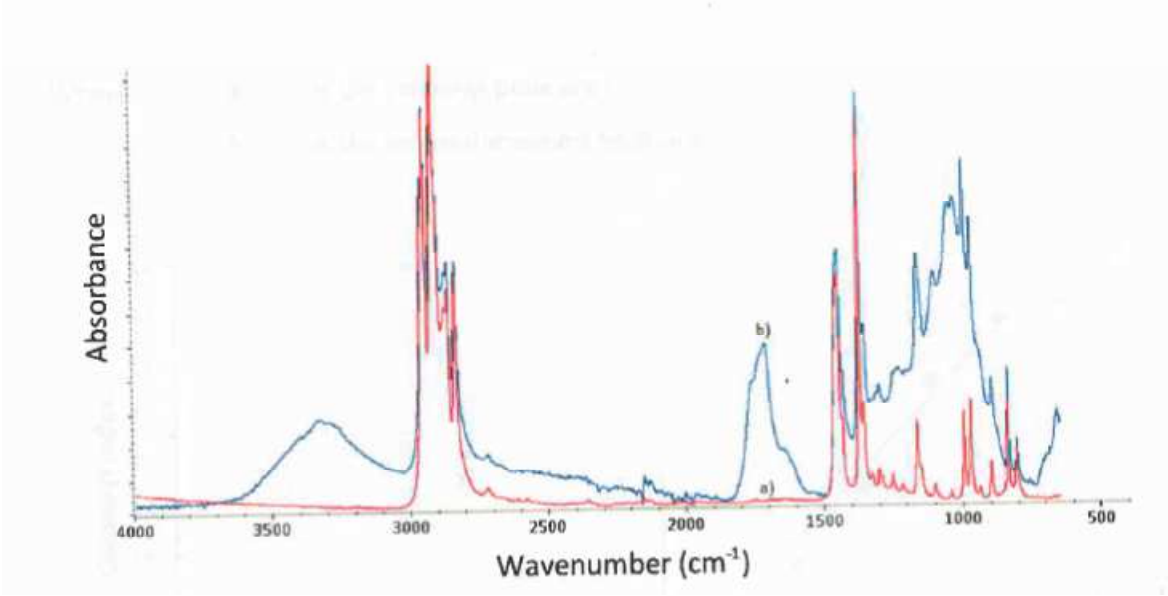


Figure 3.3: Typical infrared spectrum of PP. a) Before ageing; b) After ageing. It shows increased carbonyl and hydroperoxide concentrations [6].

Once the internal standard is chosen, the carbonyl index (CI) can be measured. This is determined by dividing the carbonyl peaks at (1500-1800 cm^{-1}) by the peak area of the internal standard (2780-3000 cm^{-1}). CI is then plotted against ageing time. The carbonyl induction time is the time taken to the onset of auto-oxidation which is manifested as an increase in rate of carbonyl growth. The time effects of the antioxidants on delaying degradation can be seen graphically.

3.1.4. Differential Scanning Calorimetry

Perhaps no fundamental property affects the physical properties of a polymer in such a general way as the crystalline content. Differential scanning calorimetry (DSC) provides a rapid method for investigation of the melting and crystallization behaviour of a polymer [79].

In a power compensation DSC instrument the sample and reference pans are individually heated, such that the rate of temperature increase of both pans remains constant. In order to

achieve this condition more power must be provided to the sample pan if an endothermic process (such as melting) is occurring. The difference in power input between the sample and reference pans is known as heat flow. A DSC instruments allows quick measurements of reaction heat, heat transitions or heat flow rates on small samples masses. The studies can be done under oxygen or under an inert atmosphere. A DSC instrument converts the temperature difference into a measurement of energy per unit mass.

The sample is contained in a metal pan and the reference is put in a similar empty pan. The pans are usually made from aluminium. The pans are placed in the DSC that features individual electrical heating elements and temperature sensors under the same and reference recepticles. The DSC head is usually purged with Nitrogen, as in most cases oxidation of the sample is to be avoided. However, an oxygen purge is sometimes used to observe the oxidation of the samples. An oxygen purge will be used in this study to assess the oxidative stability of heat aged samples of PP [80].

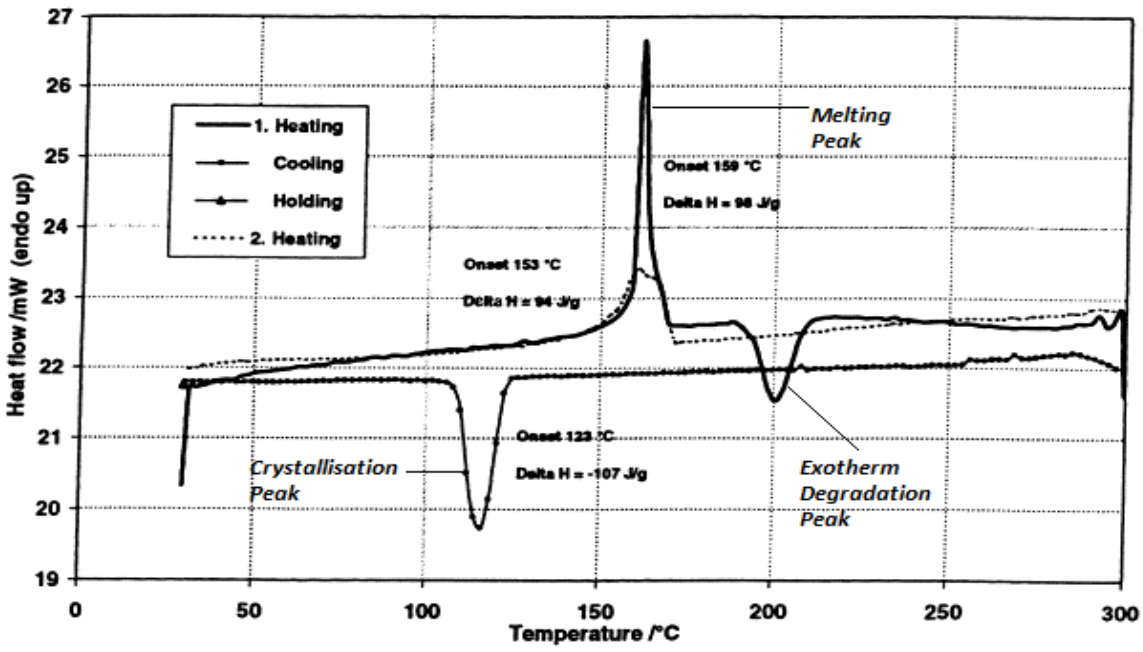


Figure 3.4: Typical DSC data showing the melting, degradation and crystallisation data for Polypropylene.

As well as the crystallisation behaviour of the polymer, DSC is also used to determine oxidation induction time (OIT) and oxidation onset temperature (OOT). These tests can give an indication of the resistance of the material to oxidative degradation and the efficiency of the stabilisers against oxidation [81]. Both OIT and OOT are well established methods to check the activity of the stabilisation system used.

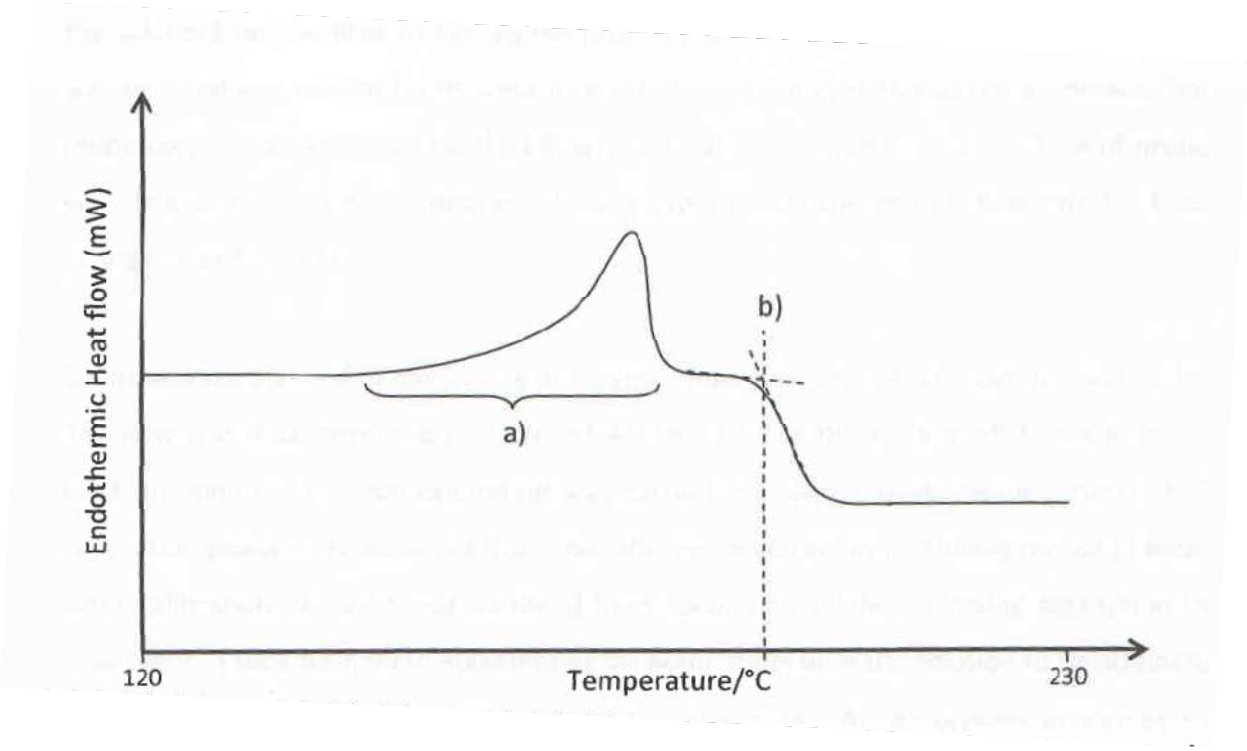


Figure 3.5: Schematic DSC trace showing how oxidation onset temperature is determined. a) Melting range of polypropylene; b) Oxidation onset temperature.

OOT tests samples are heated at a constant temperature rate in the presence of oxygen. An oxidative reaction is displayed on the thermal curve (Figure 3.5) and this is the temperature at which the polymer starts to degrade or at which oxidation begins. These measurements are quite simple and they can be used to establish suitable temperature for OIT tests.

During oxidation induction time (OIT) measurements the polymer is raised to a pre-determined temperature under nitrogen. After five minutes at this temperature, the sample atmosphere is

then changed to oxygen. The time interval between the latter switch over and the onset of the oxidation exotherm is known as the OIT. OIT can provide a relative measure of thermal oxidative stability of the polymer and rather a more accurate assessment of melt stabilization performance (Figure 3.6) [81 - 83].

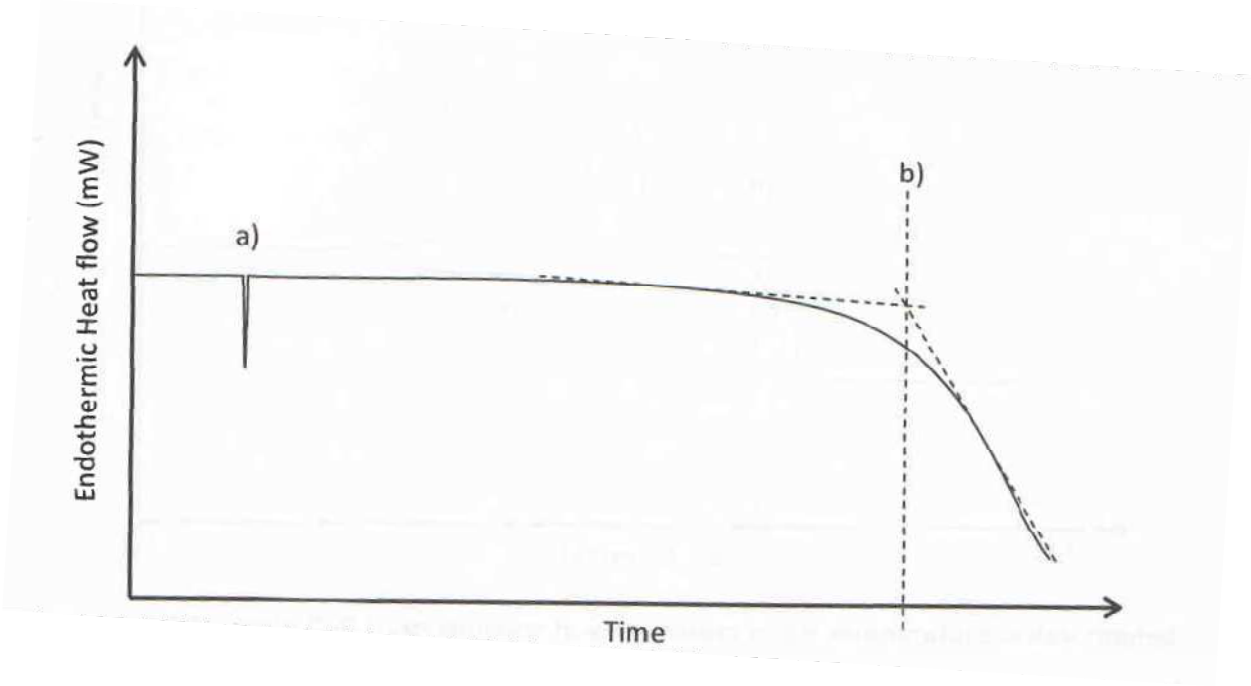


Figure 3.6: Schematic DSC trace showing how oxidation induction time is determined. a) Is the response to a change in pressure when the flow is switched from nitrogen to oxygen; b) Is the point where oxidation begins.

3.1.5 Thermogravimetric Analysis TGA

Thermogravimetric analysis measures the amount and rate of weight changes in a material as a function of temperature or time in a controlled atmosphere. These measurements are used to make measurements concernig composition and thermal stability.

The most common use of TGA is the determination of composition through the examination of the various steps in the weight loss process. Ideally a compound will show distinct weight loss

steps and they will be clearly different and defined by temperature regions where there is no activity. Depending on the measurement task, various purge gases are used for recording mass change as a function of temperature and/or time.

One of the main utilisations is for investigating degradation behaviour of filled materials. This enables polymer to decompose and the fillers to be clearly separated. Under inert conditions, i.e. in nitrogen atmosphere, most plastics degrade in a temperature range between 400°C and 600°C. However, majority of the fillers are resistant in this temperature range. Nevertheless, plasticisers and low molecular segments volatilise in a temperature range up to 400°C [84-86].

3.1.6 X-Ray Diffraction

Generally, polymers are considered as amorphous materials, however, it due to the regularly arranged polymer chains, many polymers exhibit varying amount of crystallinity and hence, can be characterised by X-ray diffraction. For many applications and the mechanical properties, which is the main area of interest for researches and manufacturers, it is important to measure the crystallinity. The crystalline domains act as a grid, and improve the performance of the material over a wide range of temperature, however too much crystallinity causes brittleness.

The X-ray diffraction (XRD) technique has been used successfully for long time in the crystallographic study of the polymers. It is usually used for the analysis of crystalline phases is solid materials, determination of the amount of crystallinity and identification of the crystallinity structure. The main advantage of the XRD is its non destructive nature of analysis.

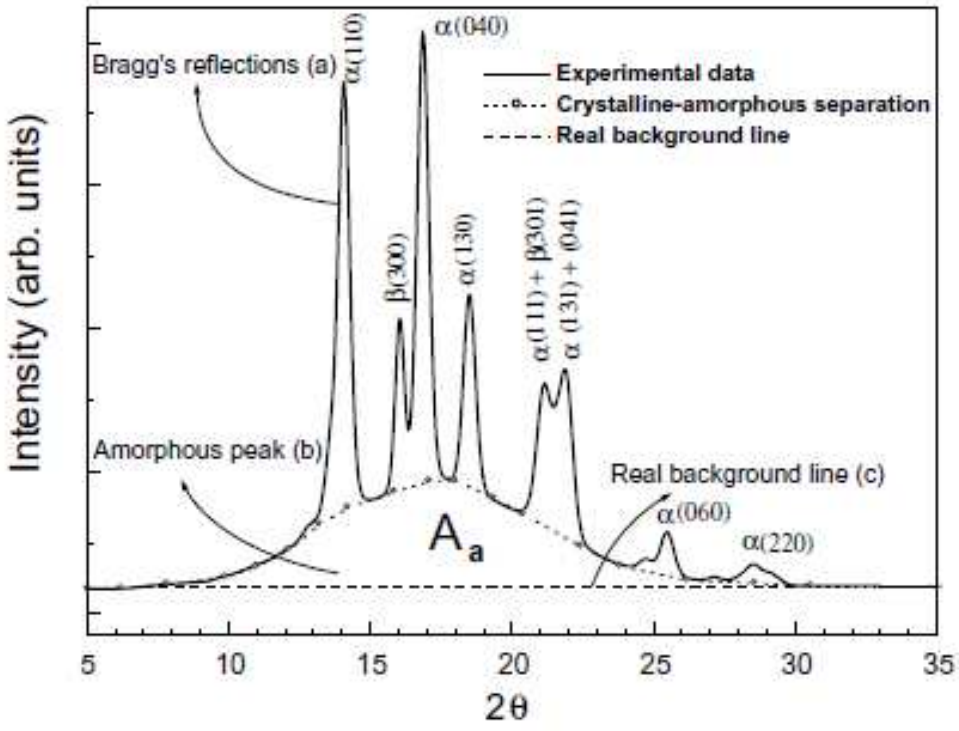


Figure 3.7: Polypropylene's X-ray diffraction graph. a) Bragg's reflection (Crystalline peaks) b) Amorphous peak c) Real background line. Both α and β forms are shown in the illustration [89].

In the analysis, the crystalline part gives sharp narrow diffraction peaks while the amorphous region gives a broad peak. The ratio of these intensities can be used to calculate the degree of crystallinity in the material. Anyway, there many ways to determinate the degree of crystallinity using the XRD. The most common method is Wide Angle X-ray Diffraction (WAXD). The intensity of X-ray scattered from the entire sample is total are under the diffraction pattern. The total intensity is divided in two zones, crystalline and amorphous, called Ic and Ia respectively. With this the crystallinity degree can be calculated with the following equation [87-90]:

$$Q = \frac{Ic}{(Ic+Ia)} \qquad \text{(I)}$$

3.2 PROCESSING TECHNIQUES

Polymer processing is a term that refers to the multitude of physical and chemical operations that involve polymers, during their manufacturing, handling, compounding or transformation into commercial products. In the next chapter it will be explained how the polymer has been prepared and moulded with different techniques such as rotational moulding, injection moulding, compression moulding, extrusion and a Haake Polydrive mixer. Each of these techniques will be described individually in this chapter.

3.2.1 Rotational Moulding

The rotational moulding (or rotomoulding (RM)) process uses the rotation of a mould in a heated chamber to form a part. The polymer (usually in powder form) particles stick to the hot walls of the mould, melt and sinter together to form a continuous skin of melt. The thickness of this skin increases until all the powder is used up. Sufficient “cook” or heating time must be allowed so that the particles can be fully sintered. If the heating time is excessive, however, degradation out-weighs any advantage gained from full sintering. RM is suitable for the formation of large and seamless parts, such as agricultural tanks. However, it can also be utilized to make small parts such as ping-pong (table tennis) balls.

RM is unique in that the polymer particles are not subjected to any shear forces. Sintering of the polymer particles is dependent on the intensity of thermal motion and mobility of the polymer chains. The latter places unique demands on the polymer. The parts made by rotational moulding can be functionally competitive with those made by other processes, and it also offers some unique processing advantages. However, rotational moulding also has some limitations.

Figure 3.8: Examples of rotational moulding products [91].

The RM process consists of four principles steps (Figure 3.8): loading, heating, cooling and unloading. The loading step begins with the weighing of a charge of the starting material which is usually a thermoplastic powder. The amount of charge is the desired mass of the finished part. The charge of the material is loaded manually into a cold mould prepared by coating the inside with a mould release agent. Then, the mould is closed and transferred into an oven where the heating cycle is done. The heating cycle is the longest cycle and is, therefore, the rate-determining step. It is common to have multiple moulds being heated together to increase the productivity of RM. These moulds must be rotating continuously during the heating and cooling cycles to achieve an adequate fusion of the powder. To obtain a complete coating of the walls by the plastic material, the moulds must be rotated about more than one axis, usually two axes. This process lasts 7 to 30 minutes. Large and thick parts may require longer heating cycles. When the plastic material has been fully fused the cooling step starts. Without stopping the rotation, the moulds are transferred to a cooling station where they are cooled as quickly as possible by spraying it with cold water or blowing air. If the cooling step is too fast some shape distortion or surface blemishing may occur. After the cooling step, moulds are transferred to an unloading station. During the unloading step, the cold part is removed mechanically or manually.

One of the main advantages of RM is the ability to make large parts with a relatively low-cost. Thanks to RM being a zero pressure process, moulds can be fabricated relatively cheaply in comparison to injection moulding or blow moulding tools. As no significant flow of the polymer occurs and cooling is relatively slow, it may be argued that rotational mouldings have very low levels of built in stress relative to injection and blow mouldings. The components that can be manufactured by this method can be of roughly similar complexity to those made by blow-moulding or thermoforming. Inserts and other metal component can be easily added to a rotational mould prior to closing the mould.

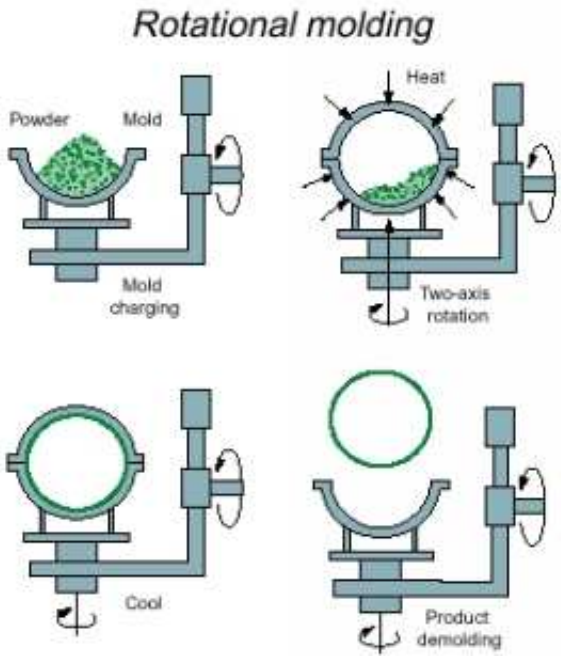


Figure 3.9: Schematic illustration of the four steps of rotational moulding.

On the other hand RM has its limitations. First of all, the parts that can be made by this method will have simple shapes and the size will be limited by the size of the oven and the cooling chamber. Parts made by injection moulding can have greater complexity and for small parts the cycle times for thermoforming and blow-moulding are much lower than those for equivalent rotational mouldings. Due to virtually zero built in stress, the mechanical characteristics of rotational mouldings are improved relative to an equivalent component produced by injection

or blow moulding or thermoforming. However, if the plastic is not fully fused / sintered in RM, the impact toughness will rapidly decrease [92].

3.2.2 Injection Moulding

This is the moulding process most used with polymers. It is a discontinuous process which consists of three parts: pressure filling of the mould, cooling and demoulding. Nowadays this application could be used with different types of polymers, such as semi-crystalline thermoplastics, thermosets, rubbers and other materials such as ceramics and metals. However, it is mostly performed with thermoplastics such as polypropylene. The injection moulding industry is expanding worldwide and besides extrusion moulding, it is the dominant plastics processing technology. Approximately one third of all plastics processed and consumed worldwide are injection moulded. Furthermore, injection moulding is the most versatile process for the manufacture of plastics with various shapes and sizes, including complex 3D shape products [93]. Automotive products, electronic devices, household items or medical equipment are some examples where injection moulded products are used.

The majority of injection moulding machines are horizontally built. However, equipment with vertical clamping or injection units is frequently used and some machines can be converted from horizontal to vertical operation [94].

In this moulding process an appropriate quantity of the polymer enters the cylinder via the feed hopper. By rotation of the screw, this charge is propelled into a heating chamber where the thermoplastic material is transformed into a viscous liquid (i.e. the polymer melt). As the screw continues to rotate the melt passes through the check ring (a one way valve) at the end of the screw, causing the screw to move backwards to give the required shot weight. Once the latter is attained, the screw moves forward, resulting in injection of the melt into the mould. It is necessary to maintain the pressure until the molten polymer solidifies. Finally, the mould is opened and the moulding then removed. The process is then repeated. The injection moulding process is schematically illustrated in Figure 3.9 [95].

The most outstanding feature of this process is the speed of production. For thermoplastic materials the whole process lasts between ten and thirty seconds because the solidification of the material is almost instantaneous. It makes injection moulding capable of doing millions of pieces in a relatively short space of time. Furthermore, pieces with complex shapes and thin thickness can be moulded with high accuracy due to the high pressure applied during the process. Because the majority of injection moulding processes are automated, only one operator is need to control multiple machines. However, injection moulding also has some disadvantages: Lots of low cost pieces such as bottles cannot be produced by injection moulding. Also the moulds are quite expensive and make that a production series with a low quantity of pieces economically unviable [96].

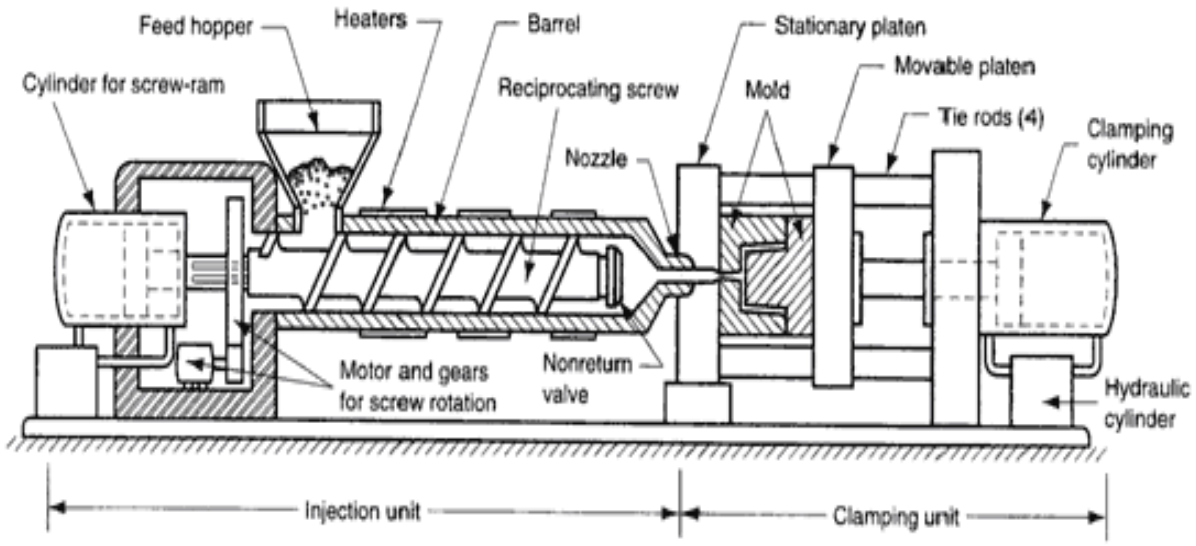


Figure 3.10: Schematic presentation of an injection moulding machine [95].

3.3.3 Compression Moulding

Compression moulding is a moulding process used most commonly for moulding thermoset materials, but it can also be used to mould thermoplastic materials if mould cooling, or an adjacent cooled press is available. When thermoplastic materials are moulded by this method, the method is sometimes called sintering. This process is used to produce specialised mouldings

with wall thicknesses of at least 15mm, which cannot be obtained by extrusion or injection moulding. Unlike extrusion and injection moulding, which use a screw for the moulding process, compression moulding involves pressing of a deformable material charged between the two halves of a heated mould. The specific moulding parameters depend on the material utilized [95]. The sintering process, or compression moulding for thermoplastic materials, consists of three steps.

During the first step, premeasured raw material called “charge” is placed inside a preheated matched-die mould. The raw material can be either sheet moulding compound (SMC), bulk moulding compound (BMC), long fibre-reinforced thermoplastic sheets (LFTs) or glass mat thermoplastics (GMT). Polypropylene is generally the resin used in thermoplastics systems such as LFT and GMT.

Once the charge is placed inside cavity, then the two halves of the mould are closed to heat the resin and pressure is applied through a hydraulic press, causing the resin flow and be squeezed into the shape of the mould cavity. The mould platens move toward each other until they meet. Due to the higher viscosity of thermoplastics compared to thermosets, higher pressures are required to make the material flow into the mould cavity [97].

The cooling step also has a significant effect on the mechanical and optical properties of semi-crystalline thermoplastics in particular. In relatively slowly crystallising semi-crystalline polymers, such as polypropylene, the amount of crystallinity is influenced by the cooling rate. Faster cooling results in lower crystalline content because the crystallites do not have time to form. High crystalline content usually increases stiffness whilst a low crystalline content favours partial flexibility, flexural fatigue life and compressibility [92].

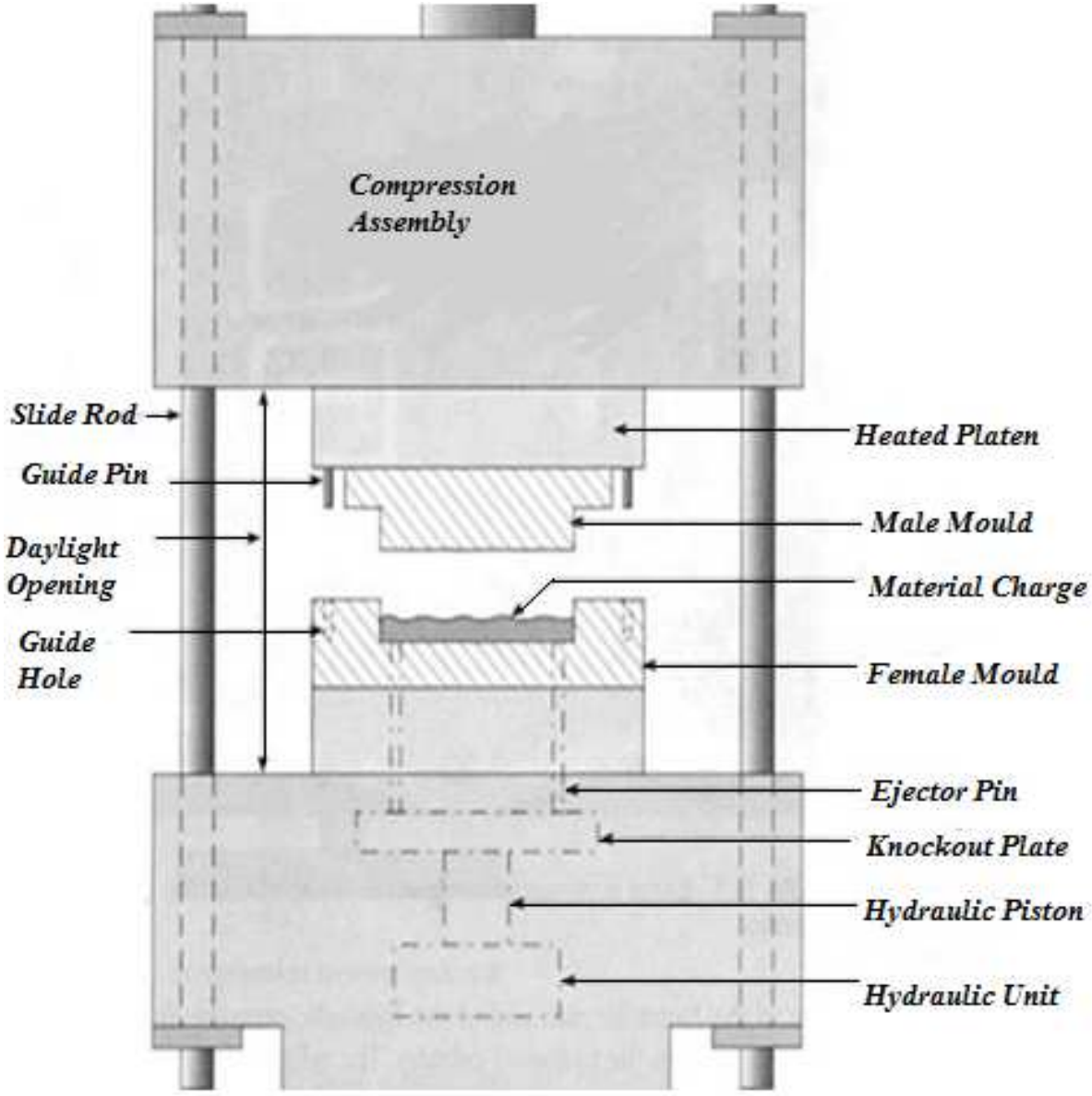


Figure 3.11: Schematic illustration of compression moulding process.

3.2.4 Extrusion Moulding

Screw extruders represent the major processing machine of the thermoplastic industry, and play an important role in many related industries [98]. The apparatus is usually fed at room temperature with resins in the form of beads, pellets or powders. During the process the

material is heated until viscous and extruded by forcing it with the screw and through a die with a defined cross-sectional shape, circular cross-section strands in the case of a compounding extruder. The strands can be cut at the die face and the melt pellets rapidly cooled as the whole assembly is immersed in the water or the strands can be fed through a cooling trough and converted to pellets using a pelletiser. Extruders are generally twin screw or single screw though melt mixing is mainly carried out using twin screw extruders [98] as is the case in this study. They can be distinguished by different characteristics, but they are usually classified by: screw geometry, screw rotation direction, number of screws and contact of screws.

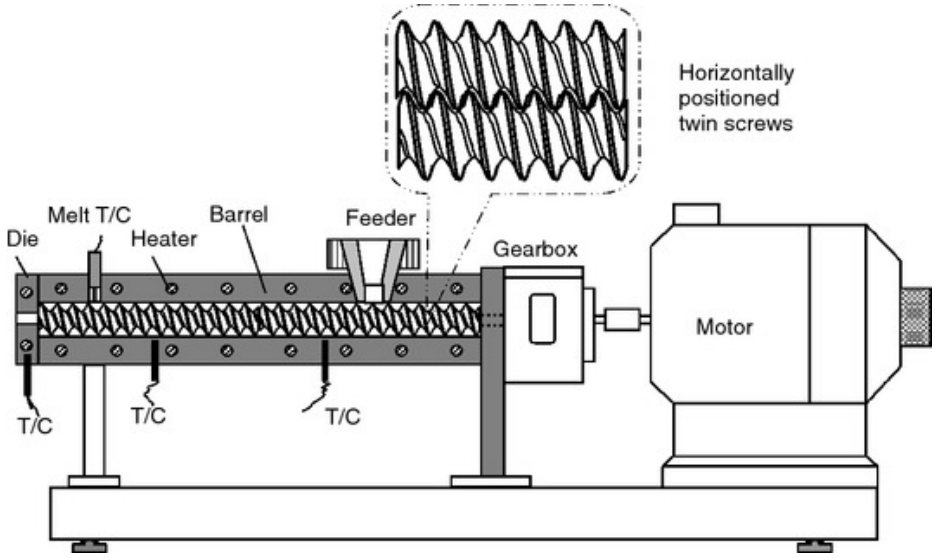


Figure 3.12: Basic diagram of a twin screw extruder [99].

Twin screw extruder operating variables are screw speed and barrel temperatures, while the design variables are the screw diameter and length expressed as a length to diameter ratio (L:D). These variables determine the residence time and available barrel surface for heat transfer. The design of the screw is the most important factor for a good quality of the extrusion.

3.2.4.1 Batch Mixing Torque Rheometer

A batch mixing toque rheometer gives the possibility to test how the materials behave during extrusion. This laboratory scale test can simulate industrial scale extrusion, so it provides adequate information for applications that require the extrusion of the material.

Figure 3.13: Different Rotors for a Thermo-Haake batch mixing torque rheometer. From left to right: Z-blade, Banbury rotors, Cam rotors and Roller rotors.

The rheomixer is an excellent machine to experiment with material before applying them on a large scale. It is provided with a twin screw which counter-rotates and a liquid/air temperature controller to simulate any type of processing. Furthermore, the torque/speed is controlled. In general these types of machines are used for the examination of the effects of various additives and the manufacturing of samples for additional testing. It also simulates the melt behaviour for extrusion optimization and tests of shear stability of different materials [100].

Figure 3.14: Illustration of a rheomixer used in laboratories [100].

4. EXPERIMENTAL

4.1 MATERIALS

The polymers used in this project were provided **ROTOMOTIVE.Ltd,** who also provided partial funding for the MSc study.

4.1.1 Polymers

During the study five different commercial brands of polypropylene were analysed.

Table 4.1: Polymer brands and some of their characteristics [101 - 104]

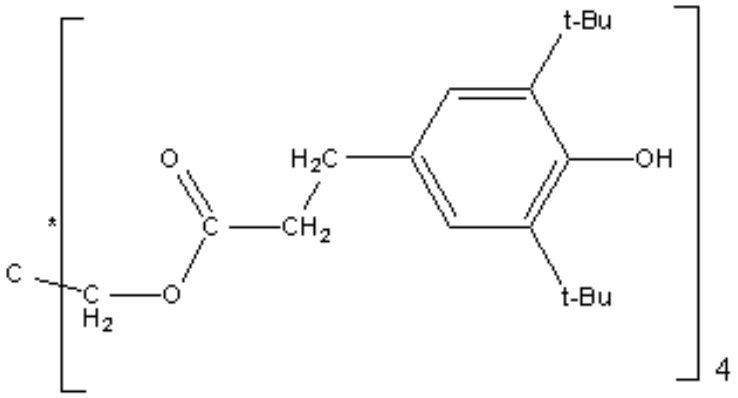
Polymer Name	***MFI (g/10min)***	***Density (g/cm^3)***	***Additional Information***
Matrix – PP35 Natural	30	0.902	Grade prepared for rotomoulding applications with good impact resistance
Icorene – 4014N	15	0.900	Stabilised polypropylene copolymer for rotomoulding applications
Unstabilised PP homopolymer Songwon Ind. S. Korea	9	0.905	Not commercially available
Bassell – Moplen PP 248R	30	0.900	Random polypropylene copolymer with good fluidity for injection moulding
Borealis – HD120MO	8	0.908	Polypropylene homopolymer with good mechanical properties for injection moulding

4.1.2 Antioxidants and Stablisers

In total five stabilisers were used in the study, one primary antioxidant, two secondary antioxidants, one HALS (Hindered Amine Light Stabliser) and one silicate, namely:

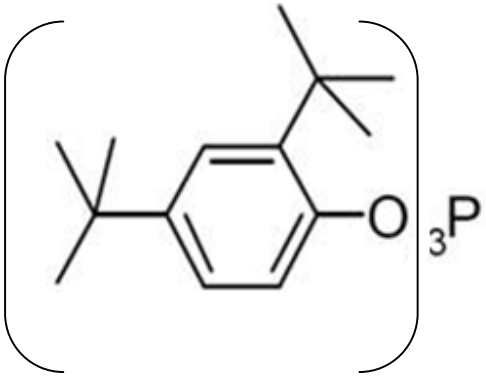
- Primary Antioxidant: Irganox 1010 (Ciba, UK)
- Secondary Anioxidants: Irgafos 168, Irganox Ps802FL (Ciba, UK)
- HALS (Hindered Amine Light Stabliser): Chirmasorb 944 (Ciba, UK)

4.1.2.1 Irganox 1010



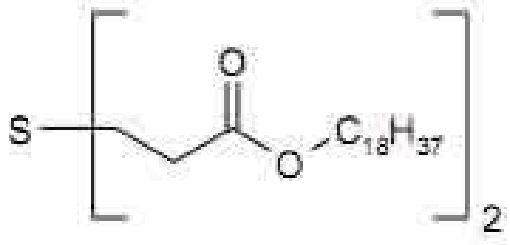
Penta-erythritol-tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) is a well-known sterically hindered phenolic antioxidant with high effectiveness, and non-discolouring characteristics. It can be used in plastics, synthetic fibres and elastomers. Its molecular weight is 1178g/mol and its melting range goes from 110°C to 125°C. Irganox 1010, because of its relative high molecular mass in comparison with BHT (butylated hydroxytoluene) which is 220.3 g/mol [105], another well known and utilised primary antioxidant, is a low migration, non-volatile antioxidant widely used in polymer industry. It is highly recommend for the stabilisation of plastics against thermo-oxidative degradation. Also, sometimes it is recommended to be combined it with secondary antioxidants [106].

4.1.2.2 Irgafos 168



Tris(2,4-di-*tert*-butylphenyl)phosphite is a highly effective, low volatility and hydrolysis resistant antioxidant for coating resins. The compound protects the resin against oxidation during processing and provides excellent protection against discolouration and change of physical properties due to excessive heat exposure. It is usually applied as a synergist with primary phenolic antioxidants like Irganox 1076 or Irganox 1010 and in case of free primary antioxidant combination with hindered amine light stabilizers. It is recognized for its good performance in industrial powder coatings, coil coatings and other industrial high bake coatings. It has a melting point of 185°C and a molecular weight of 646.9g/mol [107].

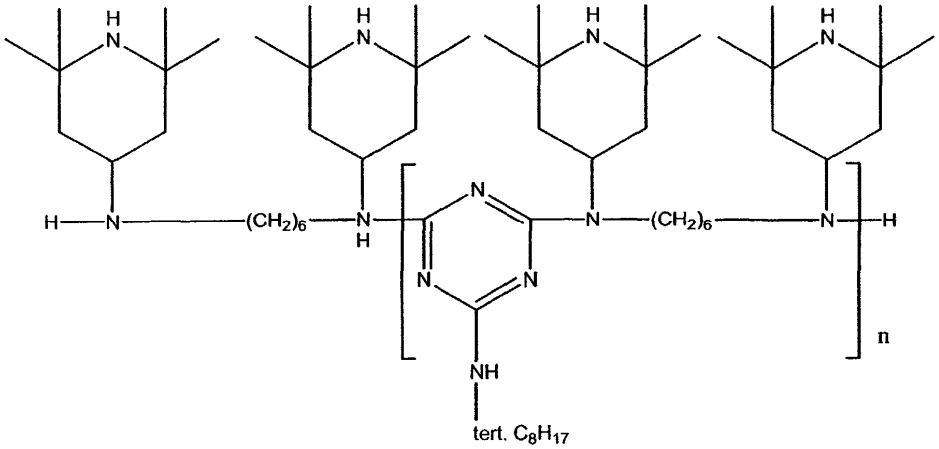
4.1.2.3 Irganox Ps802FL



Dioctadecyl 3,3'-thiodipropionate is a secondary antioxidant which is usually applied as a synergist with a primary antioxidant and provides outstanding thermal stability in polyolefins. It

functions by scavenging peroxides formed during thermal oxidative degradation of plastic and other organic materials. This compound has a melting range of 64°C to 67°C and molecular weight of 683g/mol [108, 109]

4.1.2.4 Chimassorb 944



Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-peridinyl)imino]-1,6-hexanediyl is a hindered amine light stabiliser which has a low volatility and shows excellent compatibility with polyolefins. Apart from protecting the polymer from UV light, it also gives long-term thermal oxidative stability. It has a molecular weight average between 2000-3100g/mol and its melting range is between 100°C and 135°C. Use of this stabiliser with a thio synergist can have negative effects on its efficiency [110].

4.1.3 Controlled Release Substrate

4.1.3.1 SD3128 Gel Silica

Crosfields Limited developed this silica gel, and it is a medium pore sized calcined silica gel which is known to have a large quantity of isolated silanol groups on its surface. This material also has the following characteristics:

- N_2 BET surface area: 349m^2/g
- Pore volume: 0.97cm^3/g
- Average pore diameter: 11.2nm

4.2 MATERIAL PREPARATION

In this project the materials have been prepared via a variety of methods for eventual evaluation of mechanical properties and thermal oxidative stability. In this chapter the different techniques used to measure these characteristics will be described.

4.2.1 Rotational Moulding

The machine used in this project is a Rotational Moulder Model Nº 812, made in the USA according to patent D231710. The temperatures used to rotomould the specimens were between 160°C to 230°C. Temperature and timing are regulated manually. Otherwise the samples prepared at GKN Aerospace (Portsmouth) were prepared with a industrial size machine which could manipulate two/ three moulds simultaneusly.

Figure 4.1: Picture of the rotational moulding machine utilized at Rotomotive.

The moulds are made of steel, lined with polytetrafluoroethylene, and their sizes are: 7cm x 7cm x 7 cm. Another mould was also used in this machine, and its size is: 8cm x 25cm x 8cm.

The moulds used in the industrial size machine at GKN Aerospace were hexagonal prisms and their sizes were as followings: 12.5cm (hexagon side) x 50cm (height).

4.2.2 Injection Moulding

Injection moulding was used to produce test pieces for evaluating mechanical properties such as tensile and flexural tests, as well as impact tests. The machine used to produce the pieces was a Battenfeld BA2 30CD plus. The set barrel temperature employed was 200°C and the pressure 40 Bar, while the mould temperature was set at 40°C. Test pieces were conditioned for 24 hours at room temperature before starting the tests. The test pieces had cross–sectional dimensions of 4mm x10 mm.

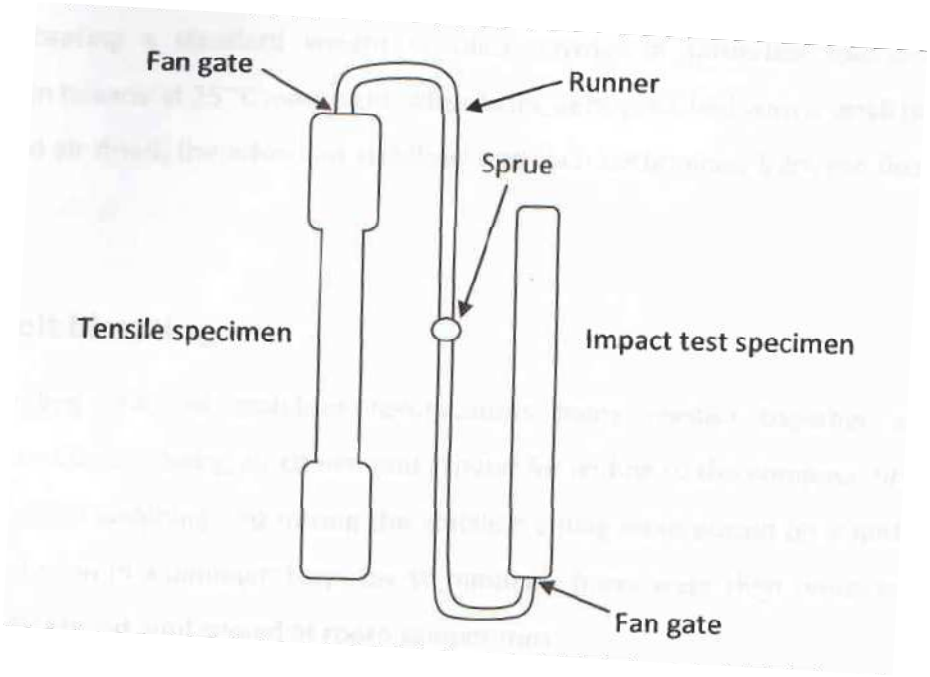


Figure 4.2: Schematic diagram of injection moulded tensile and impact test specimens, including the runner system.

4.2.3 Compression Moulding

Compression moulding was used to prepare the specimens for further carbonyl index studies and ARM falling dart impact testing. The pellets or the powder was spread over two stainless plates and were held at 180°C for 10 minutes with a pressure of 50 tonnes. Then they were pressed by 50 tonnes for another 10 minutes, but this time with a cooling system. The plaques were 3 mm thick and have sizes of 10cm x 10cm. This process was employed after processing the polymer in the Haake Rheomixer, which will be explained later in this chapter.

At Rotomotive in Northampton the compression moulding process was also used. In this case the tonnages used were different. Moulding took place using a 4 tonne hand pumped hydraulic press with electrically heated platens, whilst further pressurisation and cooling occurred in a 12 tonne press with water cooled platens. 6mm and 3mm thick plaques of 125mm x 125mm in size were produced.

4.2.4 Twin Screw Extrusion Compounding

Twin screw extrusion is a practical method for mixing stabilisers with polypropylene. The process was carried out using a Thermo-Prism TSE HC24 twin screw extruder fitted with a Brabender gravimetric feeder. The temperature profile is described in the following table 4.2. The screw speed was of 200rpm, output rate was 10kg/h and head pressure was tipically 14 Bar. The resulting molten polymer was extruded through a two-hole die and cooled in water before being pelletised with a strand dicer mill.

Table 4.2: Twin screw extruder temperature profile in °C

Feed	**Processing and Mixing**					**Die**
170	200	210	210	180	180	220

4.2.4.1 Haake Polydrive Fitted with Rheomix 600 Bowl

This method was used for the preparation and the mixing of the polymer with stabiliser before the compression moulding process. A Haake Polydrive, fitted with a Rheomix 600 mixing bowl equipped with cam blades was used to melt blend the polymers and stabilisers. Mixing time was 5 minutes at a set temperature of 180°C. The stabiliser package was added to the polymer melt after one minute of plasticisation time.

4.3 EXPERIMENTAL PROCEDURES

4.3.1 Melt Flow Rate

Melt flow rate (MFR) was measured using a melt indexer. This parameter is used to grade many commercial polymers such as HDPE, LDPE, polystyrene (PS) and PP, amongst others. A melt indexer is a variable shear stress capillary rheometer. A specified quantity of polymer is charged

into a barrel and then it is compressed to drive out the air. After two minutes of heating, a mass-loaded plunger is inserted to extrude the polymer. Because the polymers take time to get to steady-state flow, no measurements are taken during the transition period. The extruded piece produced during the transition stage is cut off and the following extrudate is collected for a specific period of time. Finally, the collected extrudate is weighed to calculate the MFR. The apparatus is illustrated in Figure 4.3.

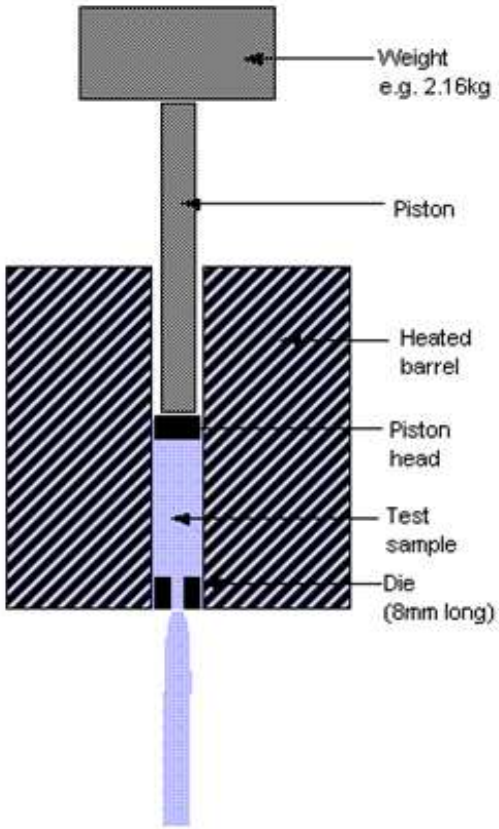


Figure 4.3: Schematic diagram of a Melt Flow Indexer

Melt flow rate is given by the weight of the extrudate in grams per ten minutes. It is performed at 190°C or 230°C (for polyethylene and polypropylene, respectively) according to ISO 1133, with a load of 2.16kg. Polymers with a high viscosity, i.e. high average molecular weight, have a

low melt flow rate, sometimes below 0.1 dg/min. For low melt index polymers experimental errors can become quite significant [111].

The melt flow rate is inversely proportional to the viscosity of a polymer at a particular temperature, so often the melt flow rate is treated as the sole indication of the processability of the polymer. While it is certainly a very important property, it is only one of the properties which control the processability, so polymers with the same melt flow index could have very different processing characteristics. This is due to the test being carried out at constant shear stress rather than constant shear rate. Polymer melt viscosity generally decreases with increasing shear rate.

4.3.2 Induction Time to Carbonyl Growth

With the measurement of the non-volatile oxidation products in the region of 1800-1500cm^{-1} it is possible to analyse the thermal degradation of the samples during the rotomoulding process. The time at which carbonyl growth begins to accelerate (i.e. the time to onset of auto-oxidation) is called the Carbonyl Induction Time (CIT), which gives an indication of the time that degradation starts on the surface of the polymer.

To determine carbonyl index for each sample of polypropylene the carbonyl peak area is divided by the reference area at 3000-2800 cm^{-1} (the area of the C-H stretching peaks).

$$CI = \frac{A\ C{=}O}{A\ C{-}H} \quad \text{(I)}$$

Note (I): Formula employed to measure the carbonyl index in polypropylene samples. AC=O is the area of the carbonyl peak, from approximately 1800-1550 cm^{-1}. AC-H is the area of the standard peak area, in this case, C-H stretching peaks, from approximately, 3000-2800 cm^{-1}.

The measurements were developed with a Nicolet Model 380 Fourier Transform Infrared Spectrometer (FTIR) with a single bounce Smart Diamond accessory. All measurements were reported in absorbance mode. It is important to mention that ATR analyses a few microns of

the surface of the polymer and not the whole polymer. Spectra were obtained with an average of 64 scans with a 4cm^{-1} resolution.

Before the samples are analysed, they have been processed with the Thermo-Haake Rheomix 600 bowl and compressed at 180°C. The cooling step was done with a 50 tonne press connected to chillers at 15°C. To measure the thermal oxidation the samples were heated in an oven at 230°C. The samples were taken from the oven periodically at intervals of 3 minutes and then the carbonyl growth was measured by ATR-FTIR technique mentioned above.

4.3.3 Mechanical Properties

4.3.3.1 Three Point Flexure

Flexural strength, also known as bend strength, is a mechanical parameter which is defined as the ability of a material to resist deformation. The flexural strength represents the highest stress experienced by the material at its moment of rupture or yield.

The two methods most commonly used for the determination of the flexural properties are the three-point and four-point bend tests. A flat rectangular sample is supported close to its ends and is centrally load by three-point bending, as can be seen in Figure 4.4.

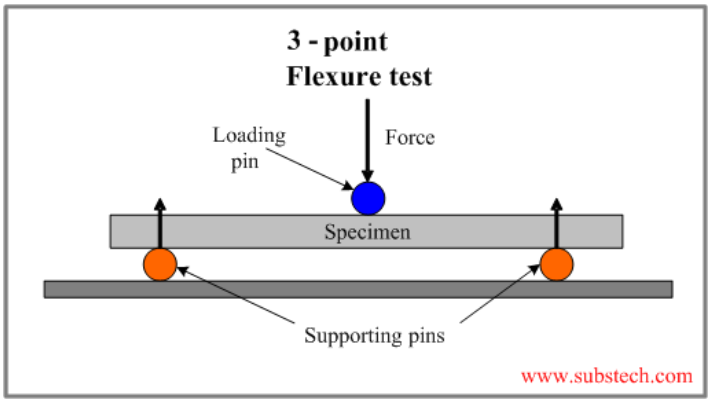


Figure 4.4: Schematic illustration of a three-point flexure test

For the calculation of the stress a formula is used which relates the force, length of the support, width and thickness to one another. Stress is indicated by **σ** and it is calculated with the following formula [112] equation (II):

$$\sigma = \frac{3FL}{2bd^2} \qquad \text{(II)}$$

Strain is calculated by a different formula (equation (III)). The symbol for the strain is **ϵ**.

$$\epsilon = \frac{6Dd}{L^2} \qquad \text{(III)}$$

Table 4.2: Table with the symbols used in strain and stress formulas and their meanings

Simbol	**Meaning**
F	Load at a given point on the load deflection curve
L	Support span, (mm)
b	Width of test beam, (mm)
d	Depth of tested beam, (mm)
D	Maximum deflection of the center of the beam, (mm)

Flexural properties were measured with Hounsfield H10KS tensometer, in this case with a 50N load range and a three point testing jig. The span between the supports is 64mm and the test speed is 5mm/min.

4.3.3.2 Tensile Strength

The stress versus strain behaviour of a material can provide a lot of insight into its properties and structure. The stress versus strain curve is obtained from load versus deflection data obtained by stretching a sample at a constant deformation rate. These curves provided the Young's Modulus, stress at yield, strain at yield, tensile strength, and the elongation at break. Stress is defined as a force per unit cross-sectional area and its basic units are N/m^2, or Pa.

Strain is a dimensionless quantity and is defined as increased in length of the specimen per unit of original length.

The ratio of stress to strain in the linear region of the stress-strain response is known as Young's Modulus and it is a characteristic property of any material. The evaluation of this parameter is particularly appropriate for polymers, because they are viscoelastic solids. However, not all polymers have the same behaviour for this test. Carwell and Nason classify polymers in five types: a) soft and weak b) hard and brittle c) soft and tough d) hard and strong e) hard and tough. Because the properties depend on time, polymers of the first type could behave in the same way as those of the fourth type if the strength is applied fast. Also, temperature is a very important factor which can completely change the behaviour of a polymer [113].

For polymers tensile strength measurements were made using a tensometer (Figure 4.5). This is an instrument which records test values on a computer to produce a stress-strain curve and calculate Young's Modulus and other tensile properties for the material. The following figure is a schematic illustration of the sample placement in a tensometer.

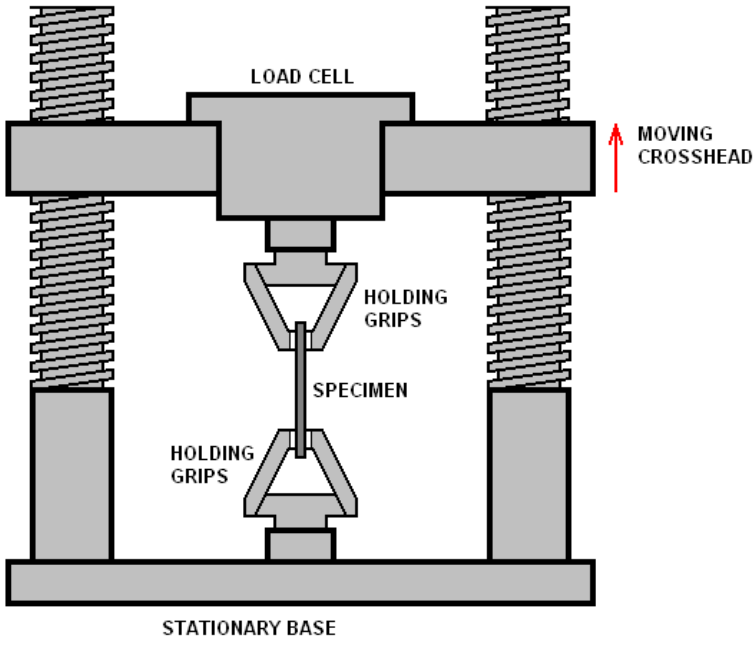


Figure 4.5: Schematic illustration of tensile test machine

Tensile properties of each sample were determined with Hounsfield H10KS tensometer fitted with a 10kN load cell, Hounsfield 100s LVDT extensometer and self-tightening wedge type grips. Test speed was set at 50mm/min. Values of stress were recorded at strains of 0.05%, 0.1% and 0.2%. The gauge lengths were 50mm. The values were determined from a batch of 10 replicates. Laboratory temperature during the test was 22.5°C.

4.3.3.3 Charpy Impact Strength

The Charpy impact test is one of the most important tests for the quality control of materials, because of its simplicity, short testing time, and low material consumption. In the Charpy impact test, a notch is sometimes cut into the specimen. Such a test is known as notched Charpy impact testing. The sample is positioned centrally on the supports, and the impact occurs on the opposite side of the notch (Figure 4.6). Stress concentration and an increase of crack propagation are achieved at the front of the crack tip. In this way, a break can be achieved even in plastic that does not break when un-notched samples are used. The radius of the notch tip has a significant influence on the impact strength. The sharpest notch used has a tip radius of 0.25 mm and the bluntest notch has a tip radius of 2 mm.

For the test, pendulums could have different energies between 0.5 J and 50 J. The energy (W) absorbed during fracture of the test piece is calculated from the difference of the impact energy required to fracture the specimen and the energy lost during a free swing of the pendulum [87].

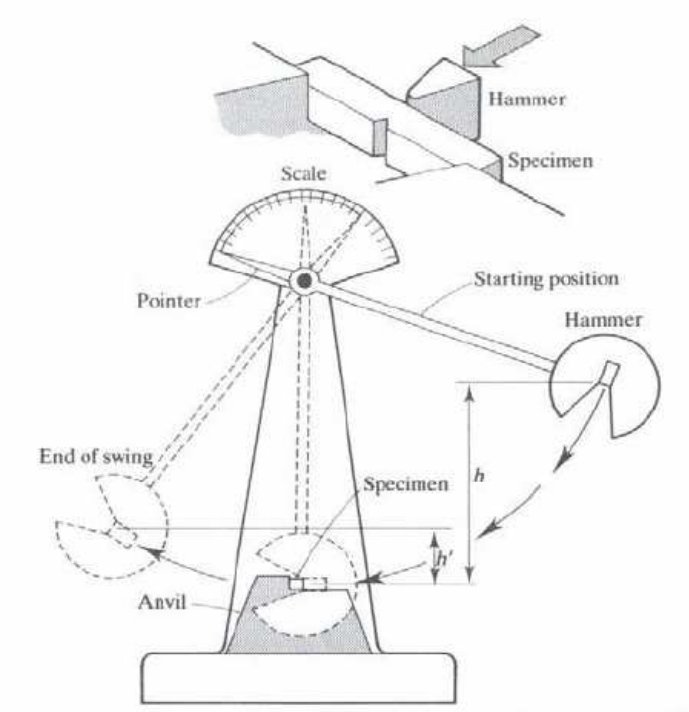


Figure 4.6: Schematic illustration of Charpy Impact test

Charpy impact tests were measured using a Zwick 5102 swinging pendulum impact testing machine, fitted with a 2J or 4J hammer. The span between the supports was 40mm. The samples were notched (to a depth of 2mm (±0.2mm)) centrally on the 4 mm side with a 0.25 mm tip radius, 45° "V" notch broaching tool. The unnotched test has been also done with a Zwick 5101 swinging pendulum impact testing machine fitted with a 50J hammer. The span between supports was 40mm like in the notched test.

4.3.3.4 Falling Weight Impact Strength Using ARM Method

This is an established method within the rotomoulding industry for the determination of the energy required to cause failure of plastic samples at low and room temperature using a falling dart. This particular variation of the falling weight impact test was designed by the Association of Rotational Moulders. Normally the test specimens should be cut from rotationally moulded components and the dart should impact the surface of the part that was in contact with the mould when it was moulded. It must be noted that a variation of the ARM test was used for this

study: instead of being rotomoulded parts the sample used were moulded by compression moulding. These samples were 3mm and 6mm thick.

The method includes four procedures: A, B, C and D. Procedures A, B and C differs only in terms of dart mass whilst procedure D differs in terms of dart mass and the geometry of the tup. Procedure A requires a 10lb (4.536kg) dart, while B requires 15 lb (6.804kg) and C requires 20lb (9.072kg) darts. During the project two additional darts were designed and manufactured especially for the PP test pieces – anticipating brittle failure at low energy. These new darts (for new procedures E and F) had masses of 5lb (2.268kg) and 2.5lb (1.134kg), respectively.

To proceed with the test, the dart is raised to the height expected to cause half of the specimens to fail. The height must be recorded. Usually the test is done with specimens removed from cold storage, but on this occasion the tests were carried out at ambient temperature. The dart falls from the raised height and the result is observed. To consider a pass there must be no visible hole in the sample. If observation of a crack is difficult, water is thrown onto the surface. Leakage of water though the sample confirms formation of a crack. If the crack is not enough to pass the water through, it will be considered as a pass. If a pass is obtained the height must be raised 5 inches, while if a failure is obtained the height must be decreased by 5 inches. Each chart should include information on specimen history, such as processing temperature, cycle time etc. For best results, 20 samples are tested and then count as the number of N. This number can be non-failure or failures, whichever is less.

Two types of failure are described. Ductile failure occurs when the dart elongates the sample and punctures a hole in the test sample. Brittle failure occurs when sample fails in a brittle manner, shattering or splitting into two or more pieces [114].

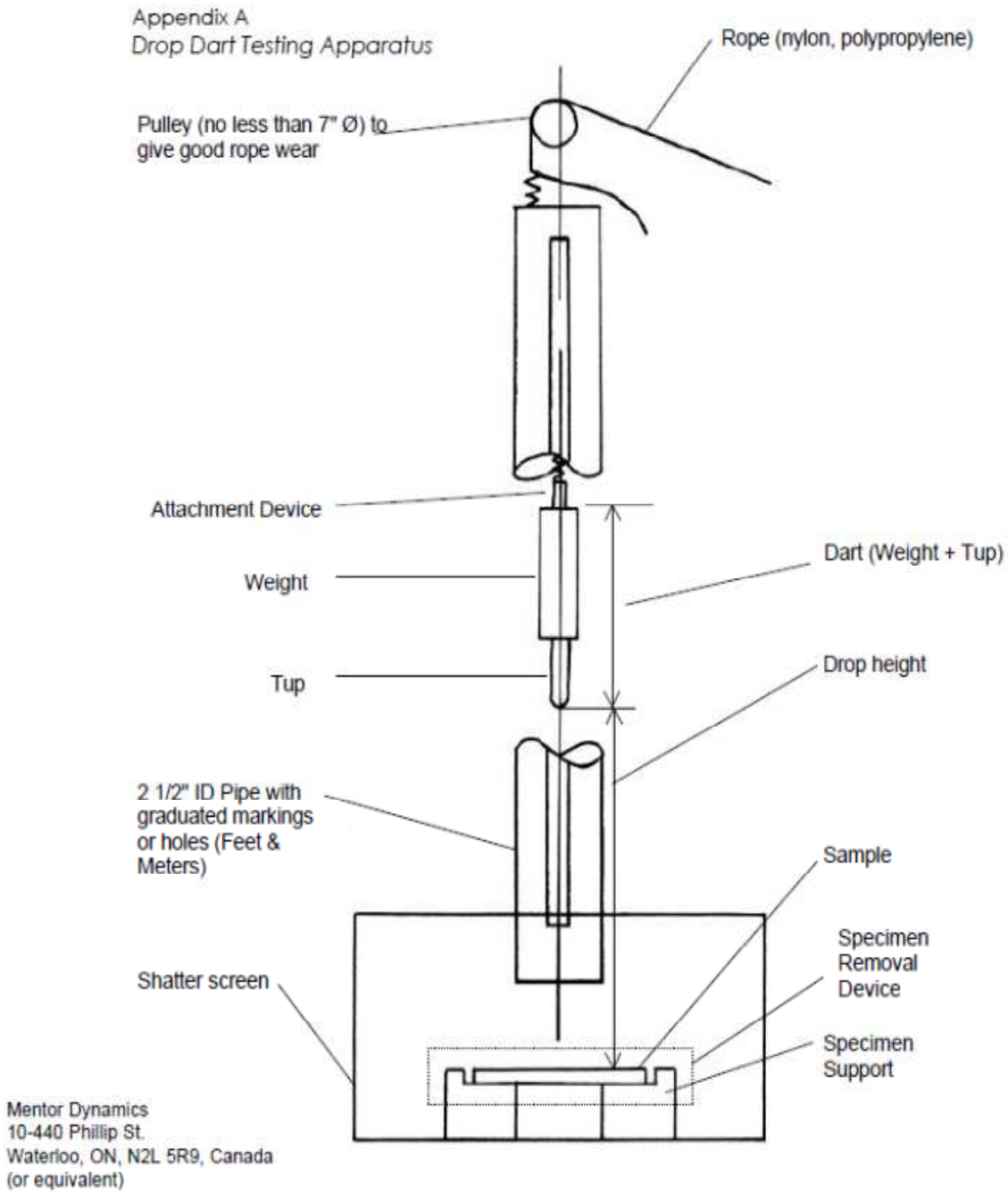


Figure 3.6: Schematic illustration of low temperature impact test apparatus.

4.3.3.5 Bulk Density and Dry Flow

The bulk density is the density of polymer particles, including the voids between particles. It is determined by filling a container of a certain volume, in this case 100ml, with the bulk material without applying any pressure or tapping it. Then the content is weighed and it is divided by the volume to obtain the bulk density.

Materials with irregular shaped particles have low bulk densities. Usually, when the bulk density is low, the mass flow rate is low as well. Bulk density at atmospheric pressure is an important parameter for polymer materials, but sometimes it is not enough and it has to be measured at different pressures and temperatures because the compressibility of particles changes. In this investigation, it will be only measured at atmospheric pressure. Dry flow tests measure the flowability of a powder. The way to measure it is by placing a standard weight, e.g. 100g, in a container and measuring the time for this to flow through an orifice. The time recorded is used as a quality control parameter [115].

4.3.4 Oxidation Induction Time and Oxidation Onset Temperature

A Perkin Elmer DSC-7 power compensation type differential scanning calorimeter was used to measure the OIT (Oxidation induction time) of the PP. Specimens were heated from 20°C to 200°C at 20°C/min. The specimens were held at this temperature for 5 minutes under a nitrogen atmosphere. After this period, the gas flow changes to oxygen and the sample is held at 200°C for 180 minutes. Oxidation was manifested as a negative deflection of the base line and the OIT is the time interval between switch over to oxygen and the onset of the oxidation. (See Figure 3.6 in Section 3.1.4)

Oxidation onset temperature (OOT) is the temperature at which the polymer starts to degrade in an oxygen atmosphere. The Perkin Elmer DSC-7 power compensation type differential scanning calorimeter was also used for this analysis, but this time samples are heated from

20°C to 300°C at 20°C/min. The temperature at which the onset of oxidation is observed is defined as the OOT. (See Figure 3.5 in Section 3.1.4)

4.3.5 Melting and Crystallisation Studies by DSC

A Perkin Elmer DSC-7 was used to analyze the melting and crystallization behaviour of the PP samples. A heat-cool-heat cycle was used to obtained data relating to the crystalline content. The temperature programme to analyze the specimens was the following:

- Heat from 20°C to 240°C at 20°C/min.
- Hold for 5 minutes at 240°C.
- Cool from 240°C to 20°C at 20°C/min.
- Hold for 2 minutes at 20°C.
- Heat from 20°C to 240°C at 20°C/min.

All segments were conducted under nitrogen and the sample mass was between 5 and 6mg.

Crimped closed aluminium pans were used for this particular DSC study. The reference was an empty pan with a crimp sealed lid.

5. RESULTS AND DISCUSSION

This study can be split into phases: The first phase is focussed on examining commercial rotational moulding grades of polypropylene (PP) in comparison with an example of a popular general purpose injection moulding grade of PP homopolymer and an unstabilised sample of PP homopolymer. The second phase concentrates on improvements of the processing stability of a selected rotational moulding grade of PP. In the latter part of the study stabilisers levels and combinations of primary and secondary antioxidants will be examined along with a method of controlling the release of the stabiliser into the formulation.

5.1 ANALYSIS OF POLYPROPYLENE SAMPLES – INCLUDING SOME COMMERCIALLY AVAILABLE ROTATIONAL MOULDING GRADES

5.1.1 Melt Flow Rate

The melt flow rate (MFR) of five different commercial polypropylenes (PPs) including several marketed as being suitable for rotational moulding was determined and summarised in Table 5.1.

The melt flow rate is inversely proportional to the average molar mass of a polymer. Polymers with a high melt viscosity are not suitable for rotational moulding because sintering of the polymer particles will be compromised as sufficient inter-penetration of chains between two neighbouring particles will not occur within a reasonable heating time. It is generally considered that for acceptable rotational moulding polyethylene the MFR should be greater than 4dg·min^{-1} (190°C/ 216kg). Therefore the suitability of particularly MMU-5014P PP homopolymer and also perhaps the Borealis-HD120MO PP homopolymer for rotational moulding applications is questionable. However, for injection moulding this parameter is not as important because during this process pressure is applied to the polymer.

Table 5.1: Melt flow rate values of PP samples provided.

	230 ℃			***190 ℃***		
	MFR in dg/min	**Average MFR**	**STD**	**MFR in dg/min**	**Average MFR**	**STD**
Matrix - PP35N	31,22			13,12		
	28,61			13,65		
	30,04	29,96	1,3	13,32	13,37	0,3
Icorene - 4014N	19,14			7,21		
	19,89			7,36		
	15,84			7,30		
	16,32	17,80	2,0		7,29	0,1
MMU - 5014P	8,57			2,19		
	10,42			2,10		
	7,99			2,11		
	9,33	9,08	1,1		2,13	0,1
Bassell - PP248R	29,96			13,35		
	31,35			13,72		
	31,09	30,80	0,7	13,30	13,46	0,2
Borealis - HD120MO	12,12			5,49		
	12,77			5,37		
	12,98			5,31		
	13,77	12,91	0,7		5,39	0,1

Table (5.1) indicates that Matrix - PP35N is the sample with the lowest average molar mass hence the lowest melt viscosity. This is followed by the fourth material in the table (Bassell - 248R). These two specimens (Bassell – 248R and Matrix – PP35N) will be the most suitable for the rotational moulding. These results are the same at both temperatures 190°C and 230°C. The corresponding decreases in melt flow index at both temperatures are shown in Table 5.1.

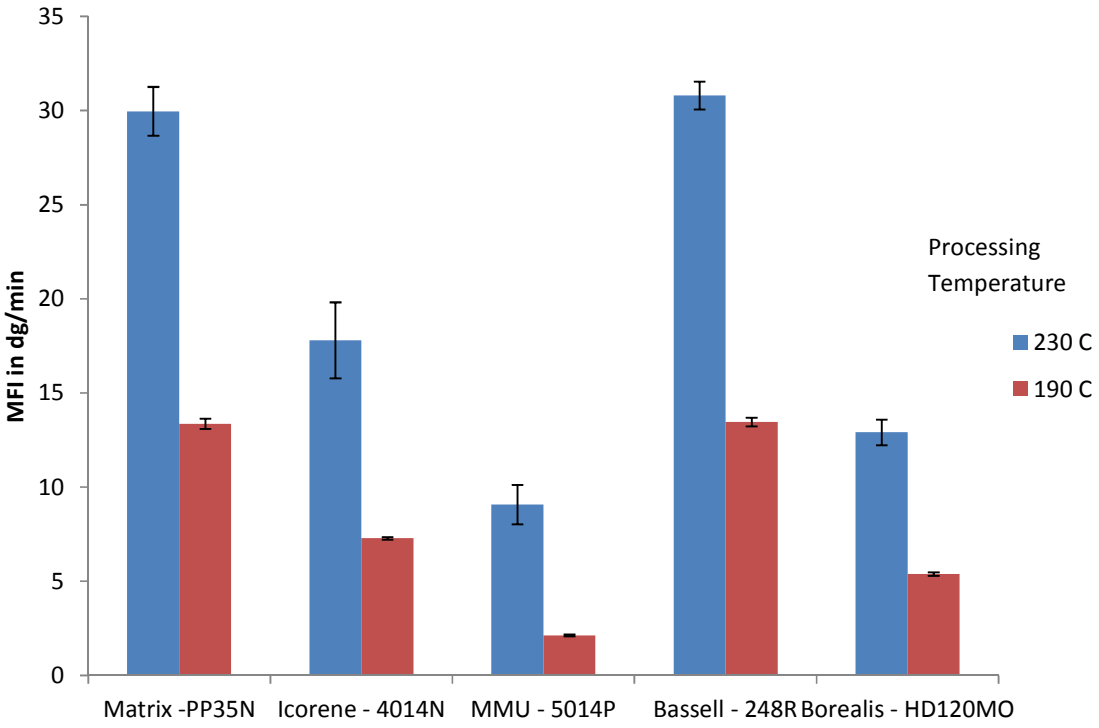


Figure 5.1: Graphic illustration of MFR in dg min^{-1} and temperature.

5.1.2 Induction Time to Carbonyl Growth

The five PPs were rotomoulded for different cook times in order to see how the level of oxidation of the samples increases as a function of cook time. The amount of oxidation is measured via ATR-FTIR determination of the relative amount of non-volatile carbonyl compounds. This test is only done in four of the five samples. Sample MMU – 5014P has been excluded from this test due to it being an unstabilised sample; its poor stability will be shown in further tests discussed in this chapter.

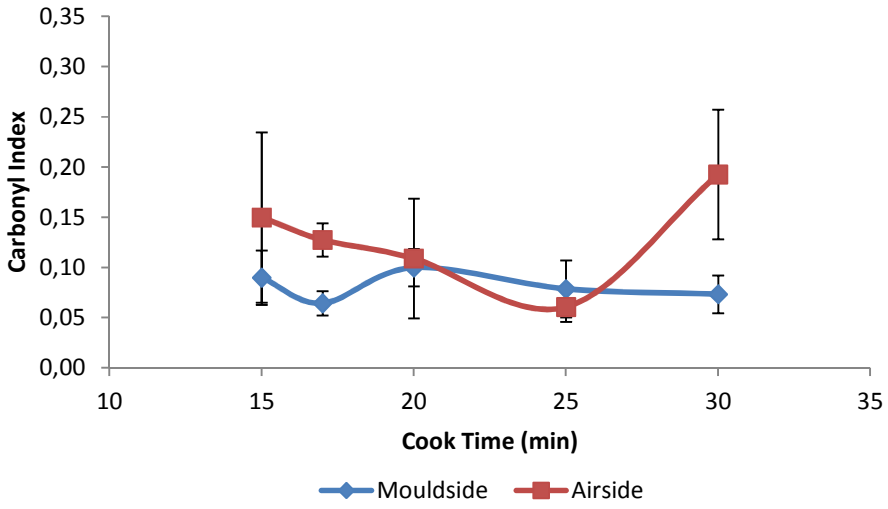


Figure 5.2: Graphic illustration of the carbonyl index for sample Matrix – PP 35N. Both sides of the moulds are plotted on the graph.

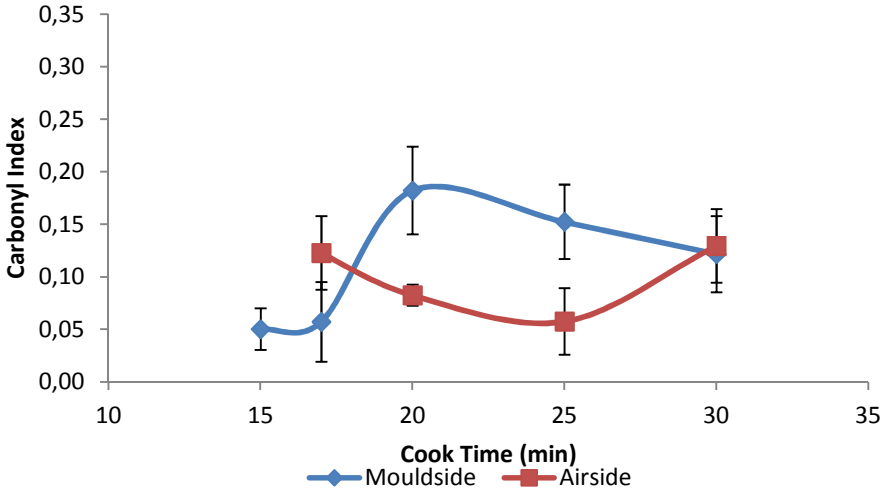


Figure 5.3: Graphic illustration of the carbonyl index for sample Icorene – 4014N. Both sides of the moulds are plotted on the graph.

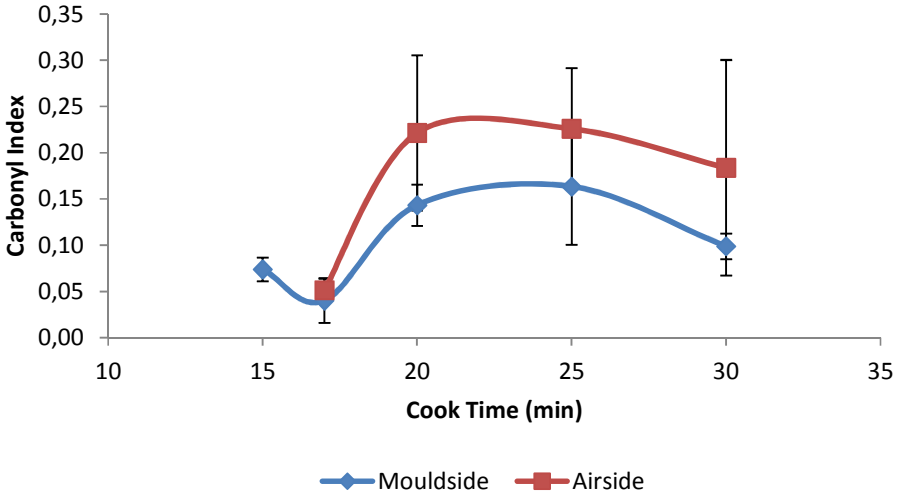


Figure 5.4: Graphic illustration of the carbonyl index for sample Bassell – 248R. Both sides of the moulds are plotted on the graph.

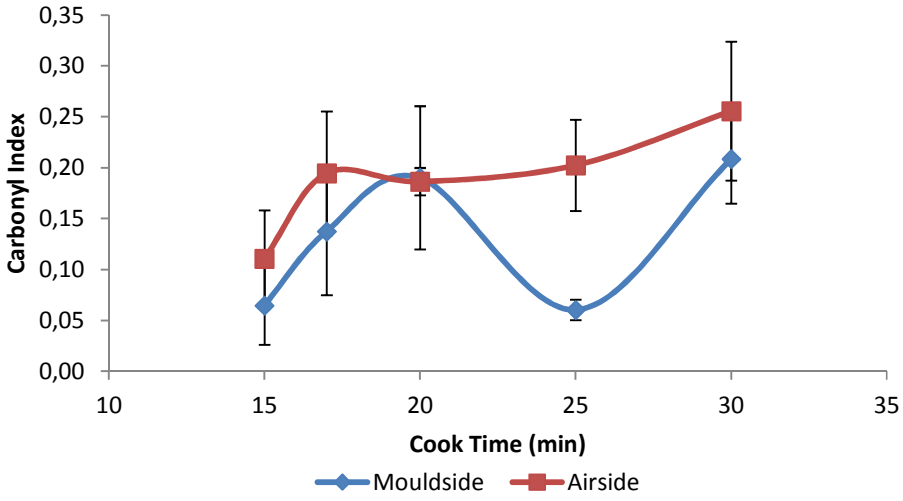


Figure 5.5: Graphic illustration of the carbonyl index for sample Borealis – HD120MO. Both sides of the moulds are plotted on the graph.

Inspection of Figures 5.2-5.5, indicates that the oxidation of some of the PP samples during rotational moulding shows very different behaviour to polyethylene (PE) when processed in the

same way. In PE rotational mouldings, the outer surface of the moulding which is in contact with the mould surface (known as the mould side (MS)) shows slow / minimal oxidation whilst the inside surface of the moulding which is in contact with air (known as the air side (AS)) shows rapid oxidation, once the stabiliser package has been consumed [59]. However, the trends observed for the PP samples still give valuable information about the polymers.

Normal (PE – like) behaviour was observed for Borealis – HD120MO and Bassell – 248R. However, Icorene – 4014N behaves in a clearly different way from the expected, with the MS being more oxidised than the AS for a significant part of cooking period. Moreover, Matrix – PP35N does have a clear trend to relate it with one behaviour or the other.

There are some reasons for these results. One of the reasons could be that during shorter cook times there is insufficient time for the stabilisers to evaporate. Usually, stabilisers have hydroperoxides, peroxides and other chemical groups which have carbonyl groups that increase the CI of the polymeric sample. The second reason could be that the number of measurements for each specimen were not enough to get a reasonable representative and conclusive result. Each specimen has been analysed three times for both sides, which is a very small area analysed for the whole mould. The third reason could be that the surface analysed is not flat enough to make good contact with the ATR instrument which results in inaccurate results.

Despite the unexpected results, the graphs show that sample Matrix – PP35N and Icorene – 4014N have better resistance against thermal degradation as the carbonyl index is lower than in samples Bassell – 248R and Borealis – HD120MO. As the two former samples show generally slower oxidation as measured by carbonyl growth they are arguably more suitable for rotomoulding than the latter two. This was an expected observation because Matrix – PP35N and Icorene – 4014N are formulated for rotomoulding.

5.1.3 Crystallinity Studies

5.1.3.1 Differential Scanning Calorymetry

Crystallinity studies of the material were done by DSC with a Heat-Cool-Heat cycle method. The results obtained in the various stages are given in Tables 5.2-5.4.

Table 5.2: Results of the first heat of the DSC (differential scanning calorimetry)

SAMPLE	*(Tmo) α °C*	*(Tmo) β °C*	*(Tmp) α °C*	*(Tmp) β °C*	*(Xc) α (%)*	*(Xc) β (%)*
MATRIX-PP35N	148,9		163,0		35,5	
2nd peak	101,4		111,0		0,3	
Icorene-4014N	124,0	89,9	141,0	129,17	21,6	26,8
MMU-5014P	150,9		162,7		38,1	
Bassell-248R	135,3		145,3		26,4	
Borealis-HD120MO	153,4		164,3		46,5	

- *Tmo = Onset of melting temperature*
- *Tmp = melting peak temperature*
- *Xc = Crystallinity content*
- *2nd Peak = Probably PE*
- *Value of enthalpy of α-PP, 209 J/g*
- *Value of enthalpy of β-PP, 168,5 J/g*
- *Value of enthalphy of HDPE, 277J/g*

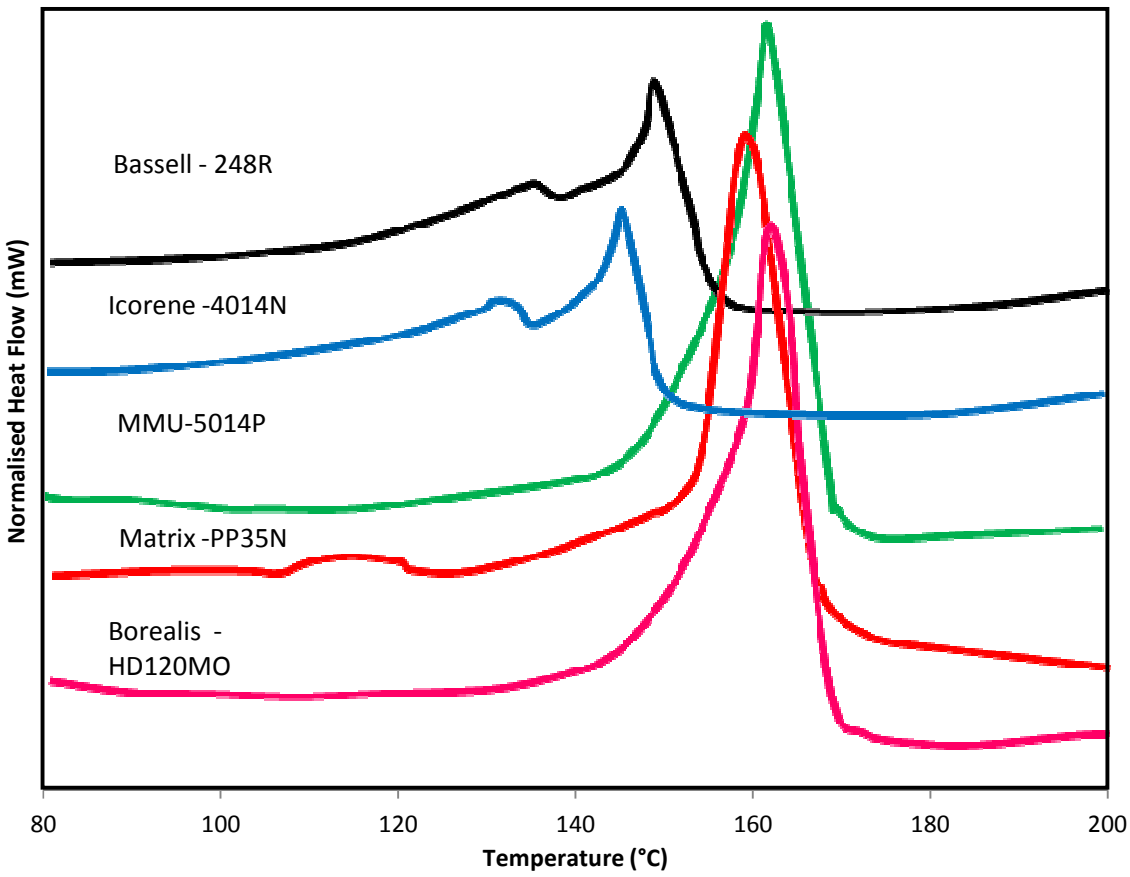


Figure 5.6: Graphic illustration of the DSC first heat of the different samples. The heat flow (mW) has been normalised.

Table 5.3: Results of the cooling of the DSC

SAMPLE	*T co (°C)*	*Tcp (°C)*	*Xc (%)*
Matrix-PP35N	111,1	105,6	38,1
2nd peak	90,2	87,9	0,4
Icorene - 4014N	115,2	110,3	22,8
MMU-5014P	112,0	104,6	40,8
Bassell-248R	116,1	110,9	28,8
Borealis-HD120MO	109,5	110,8	46,6

- *Tco = Onset of crystallisation*
- *Tcp = Crystallisation Peak*
- *Xc = Cystalline content*

Table 5.4: Results of the second heat of the DSC

SAMPLE	*(Tmo) α °C*	*(Tmo) β °C*	*(Tmp) α °C*	*(Tmp) β °C*	*(Xc) α (%)*	*(Xc) β (%)*
Matrix-PP35N	153,6		159,4		35,5	
2nd peak	105,0		112,1		0,3	
Icorene-4014N	134,7	85,0	144,4	131,7	23,8	29,5
MMU-5014P	152,9		159,7		41,2	
Bassell-248R	138,5	91,7	148,1	134,2	29,0	36,0
Borealis-HD120MO	154,3		163,1		44,0	

Some of the mechanical properties of polymers are related to the crystalline content of the sample. The tensile strength, flexural strength and the impact strength are some of the properties related to the crystalline content. DSC measurement revealed the melting and crystallisation characteristics of the composites under non-isothermal conditions.

The DSC data has to be considered together with the X-ray diffraction as the DSC data for some of the samples appears to indicate the presence of the beta crystalline form of PP. The latter usually has a double melting peak (143 and 151 °C) and the hexagonal unit cell gives a reflection peak for the (300) reflection at 16°. The latter was absent thereby indicating that the low melting temperature was due to low lamellar thickness rather than β-PP. Matrix - PP35N a second peak occurs, but it is not characteristic of the β structure, so it is probably PE. The formulation may contain a PP block copolymer or plastomer type material which is a highly branched polyethylene. The only samples with a melting point much lower than that of a normal PP homopolymer are Icorene - 4014N and Bassell – 248R.

The samples with the highest crystalline content are MMU - 5014P and Borealis – HD120MO and are typical PP homopolymers. These samples are likely to have the highest stiffness and lowest impact strength (as discussed in future chapters on mechanical properties (Section 5.1.5)). Matrix - PP35N has the second highest crystalline content. Icorene - 4014P has the lowest crystalline content.

It is important to understand the crystalline structures of polymers because it is the significant factor that determines the mechanical properties.

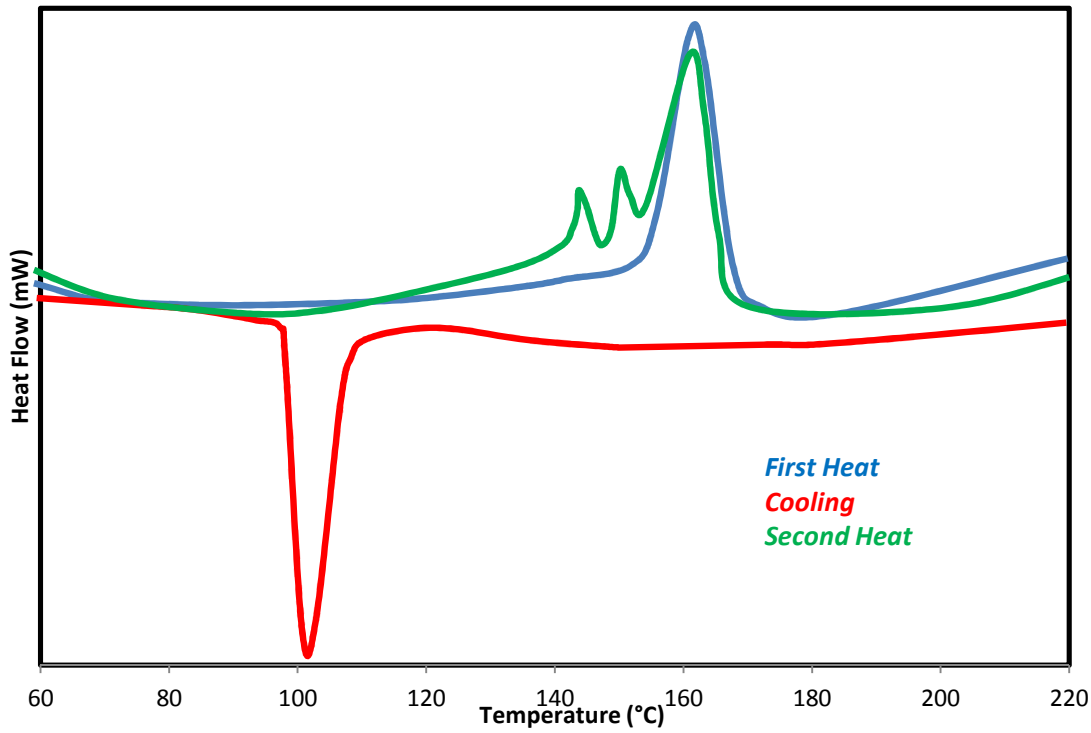


Figure 5.7: Graphic illustration of the complete DSC cycle for sample MMU – 5014P.

5.1.3.2 X-Ray Diffraction

X-ray diffraction method was also employed to examine the crystal structure of the samples.

The graphs plot the intensity against the diffraction angle 2θ, thus, the samples with the highest intensity in their peaks will be the most crystalline ones. However, this method cannot provide an exact amount of the crystallinity without the integration of the peaks.

The X-ray diffraction patterns for the five polypropylenes are stacked in Figure 5.8 it is immediately apparent that there is no β-PP present, all the reflection peaks indicate the commonly encountered alpha form of PP. The intensity of the peaks does vary however; the Bassell - 248R and Icorene – 4014N have both low intensity reflection peaks and low melting points, together these observations indicate a lower lamellar thickness than typical of a PP

homopolymer. It is highly likely that this reduced lamellar thickness and consequently low (T_m) is the result of carefully controlled copolymerisation. Matrix – PP35N, MMU – 5014P and Borealis – HD120MO have sharper and more intense reflection peaks this observation is entirely consistent with the higher crystalline content and T_m of these samples. Having higher crystallinity degree also affects to the degradation. For semicrystalline polymers degradation mainly occurs in the amorphous region, the oxygen diffuses through it causing damage at the spherulite boundaries. Because of this process, highly crystalline materials will be damage much more due to oxidation of the spherullites than the lower crystalline materials. Hence, a highly crystalline polymer with lower tertiary sites oxidises slower than a lower crystallinity degree, but the physical degradation by small amounts of oxidation is greater in the highly crystalline polymer.

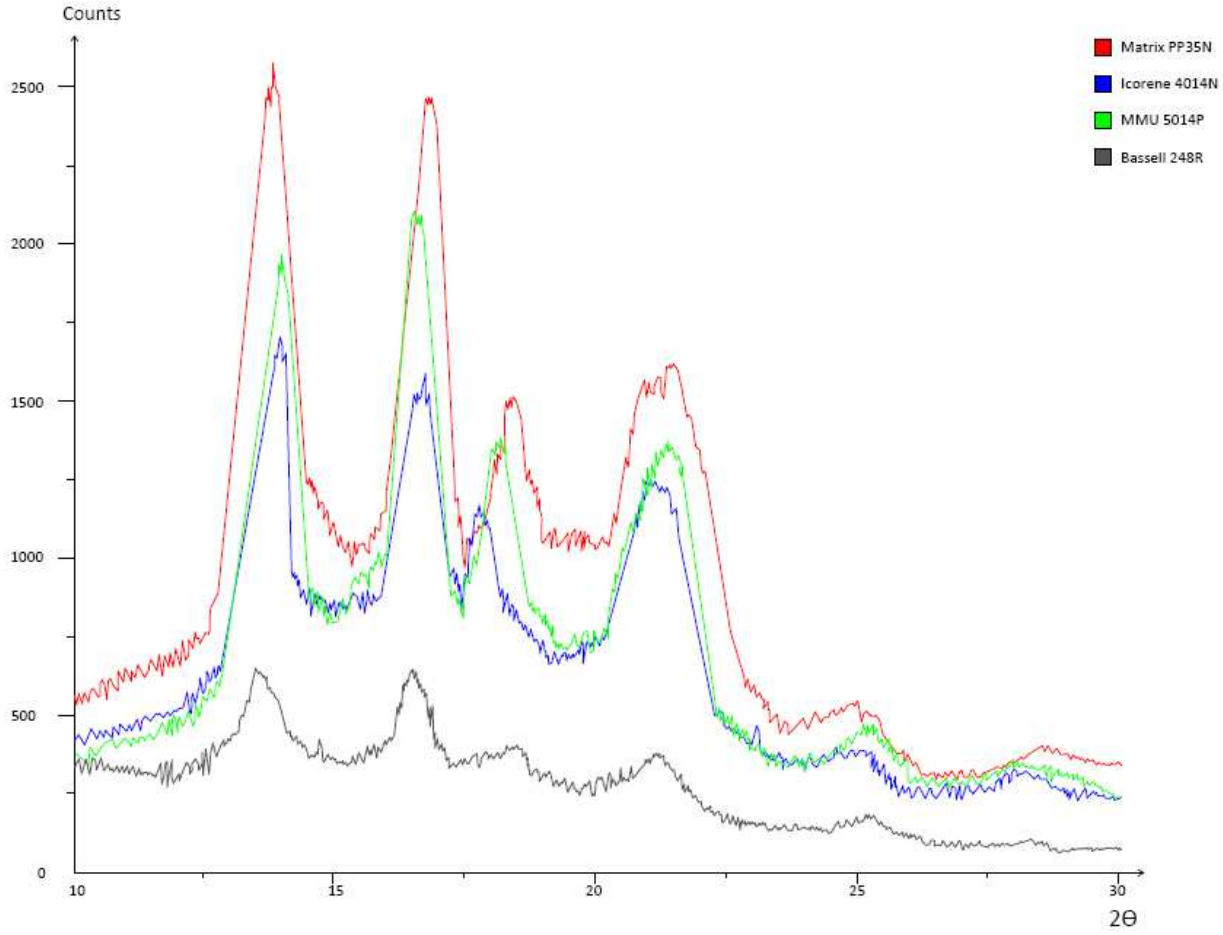


Figure 5.8: X-ray diffraction patterns of the PP samples provided.

5.1.4 Degradation Studies

5.1.4.1 Oxidation Onset Temperature

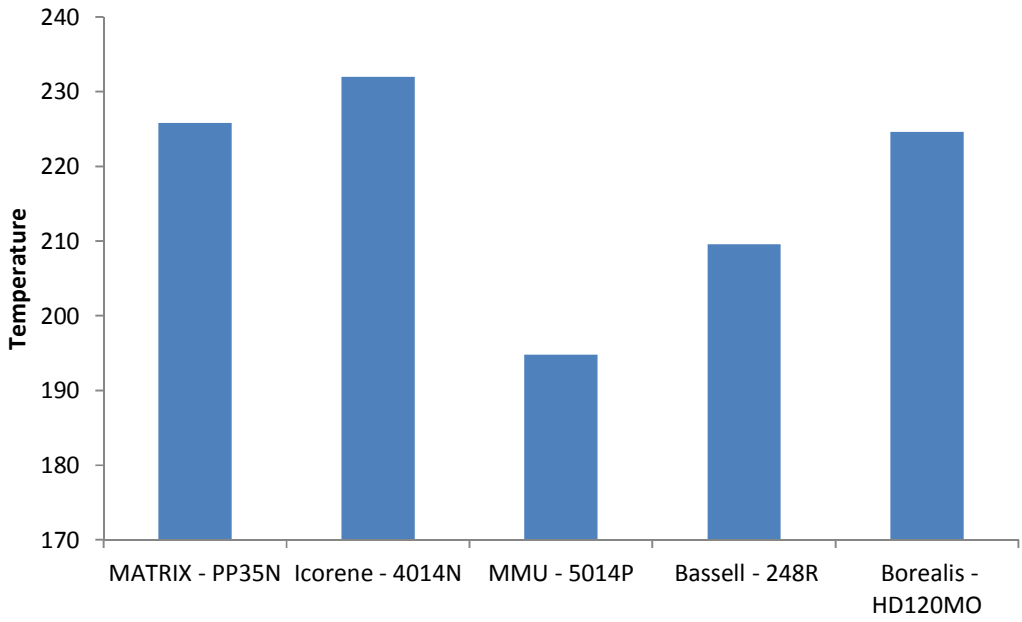


Figure 5.9: Oxidation Onset Temperature (OOT) data for the PP samples provided.

Oxidation Onset Temperature (OOT) is often used to determinate a suitable temperature at which to conduct oxidation induction time measurements. OOT nevertheless can provide rough assessment of relative melt stability performance. It provides the temperature at which the polymers start to degrade.

Figure 5.9, indicates that Icorene – 4014N has the highest OOT followed by Matrix – PP35N. This specimen starts to degrade after 220 °C and Icorene – 4014N even starts after 230 °C. These temperatures are rarely exceeded in polypropylene rotomoulding, so these samples appear to be well formulated, at least in terms of the stabilisation package which consists on a combination of additives and polymer structure. On the other hand, Bassell - 248R does not even reach 210°C, which shows that stabilisation is necessary. Even more, specimen MMU – 5014P, barely exceeds 190 °C a very poor result – not surprising considering the absence of any stabiliser.

5.1.4.2 Oxidation Induction Time

The results of the Oxidation Induction Time (OIT) of the various polymers measured at 200°C, is displayed graphically in figure 5.10.

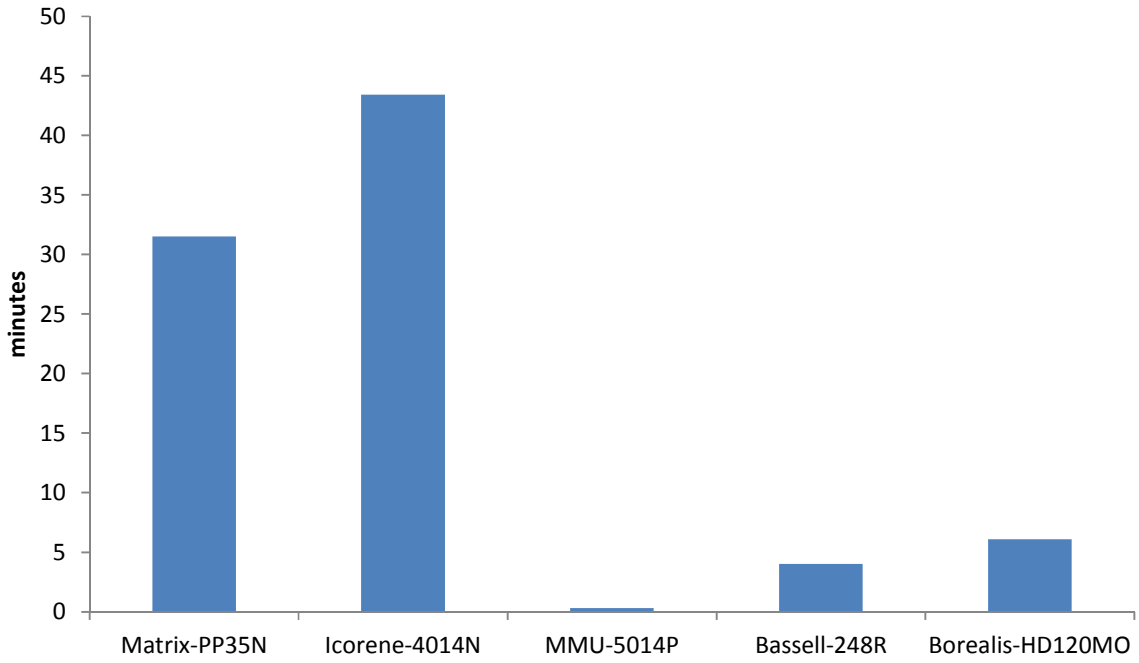


Figure 5.10: Graphic illustration of the Oxidation Induction Time in minutes at the temperature of 200°C.

Oxidation induction time data can be a good indication of how well a polymer is stabilised when in the melt state.

As the graphs show, Icorene - 4014N has the best behaviour, while MMU - 5014P and Bassell - PP 248R are very weak against thermal oxidation. Matrix – PP35N and Borealis – HD120M do not have as good resistance as Icorene - 4014N, but they can resist elevated temperatures for quite a long period of time.

As indicated in Figure 5.10, Icorene -4014N shows the highest level of stabilisation, followed by the Matrix – PP35N; these observations are expected because these PPs have been formulated for rotational moulding. The formulators have therefore done their job relatively well. On the

other hand, Bassell - PP248R and Borealis – HD120MO show much lower levels of stability at 200 °C this is again as expected as these PPs are formulated for injection moulding. In the latter process the polymer is in the melt state in a closed barrel for a few minutes only. The unstabilised sample MMU – 5014P has almost zero stability at 200 °C and thus shows vital importance of stabilisers in PP based formulations.

Oxidation induction time measurements have been taken for the specimens after being rotomoulded for 30 minutes in a Model 812 Rotational Moulding Model, as specified in chapter 4.2.1. The OIT data provides a relative measure of the amount of stabiliser is remaining in the polymer. Measurements have been taken from both sides of the moulds, airside and mouldside.

The results show that the OIT of every sample after being rotomoulded for 30 minutes is less than without being processed, which is an expected result. In all cases, the airside of the mould is more degraded than the mouldside. This is because the airside is in contact with oxygen, which accelerates the degradation of the polymer.

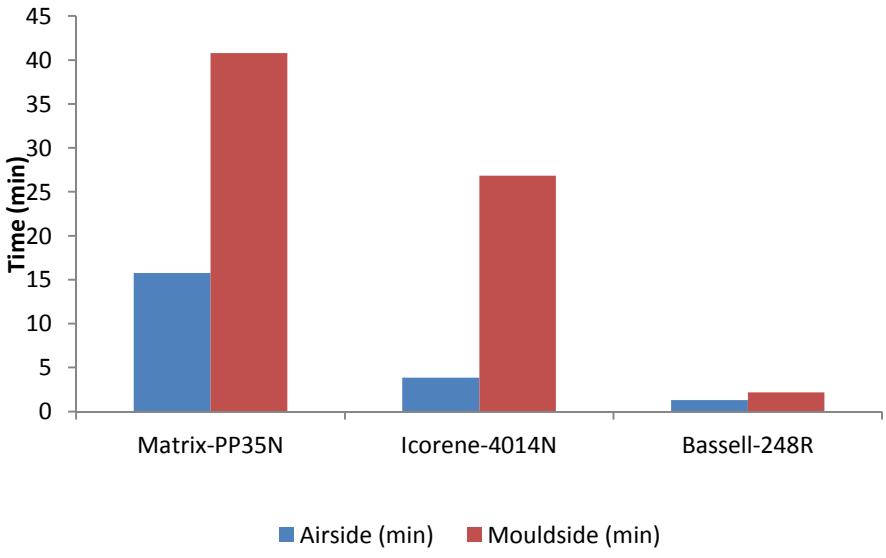


Figure 5.11: Graphic illustration of the OIT for rotomoulded samples. Samples were rotomoulded for 30 minutes.

Note: Samples MMU-5014P and Borelis-HD120MO were not measured due to their poor resistance against thermal degradation.

As Figure 5.11 shows, the specimen with the best behaviour is Matrix – PP35N, followed by Icorene – 4014N, an observation being entirely consistent with these PPs being formulated for rotational moulding. Bassell – 248R has very poor resistance for both airside and mouldside, so it needs additional stabilisation in order to make it suitable for rotomoulding applications.

5.1.5: Mechanical Properties

5.1.5.1 Three Point Bend Flexural Testing

Flexural strength is the resistance of a material to bend. With the standard three point bend experiment, flexural modulus and flexural strength can be calculated. Flexural modulus is a measure of the stiffness of a material under flexural loading. These properties can also correlate with tensile strength and they are very important in engineering and construction.

The test will provide information about the stiffness of the material. Flexural modulus was determined using the Hounsfield Q-Mat software.

The following flexural properties of the samples were determined:

1. Flexural Modulus via linear regression of the first 100 load – deflection data points.
2. Secant modulus taken between 0 and 1 % strain.
3. Flexural yield strength.

Temperature is a factor to take into account at the time of measuring these properties. In this case the laboratory temperature was 22.5°C.

The results obtained for testing the various polypropylene materials are given in Table 5.5.

Table 5.5: Results of Flexural Modulus, Secant Modulus between 0 and 1% of strain and flexural yield strength.

	FM #100 in GPa	SM 1% Strain in GPa	FYS in MPa
Matrix - PP35N	0,91	0,89	26,80
Icorene - 4014N	0,64	0,62	20,51
MMU - 5014P	1,23	1,19	35,42
Bassell - 248R	0,83	0,87	27,32
Borealis - HD120MO	1,80	1,79	60,03

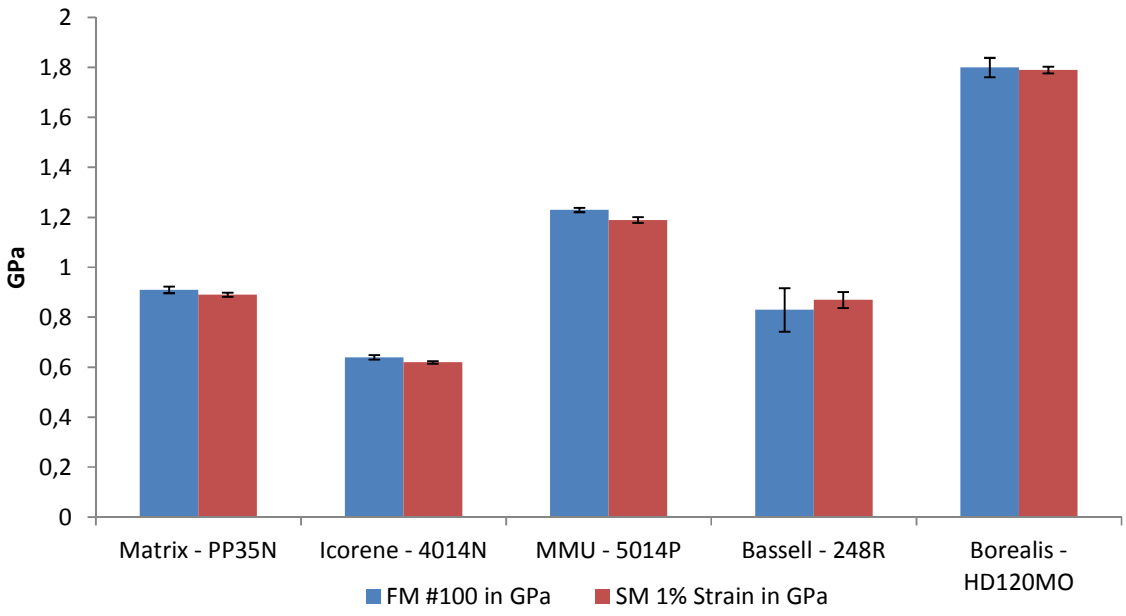


Figure 5.12: Graphic illustration of the Flexural Modulus (obtained from the slope of the first 100 data points after toe correction) and the Secant Modulus at 1% of Strain in GPa.

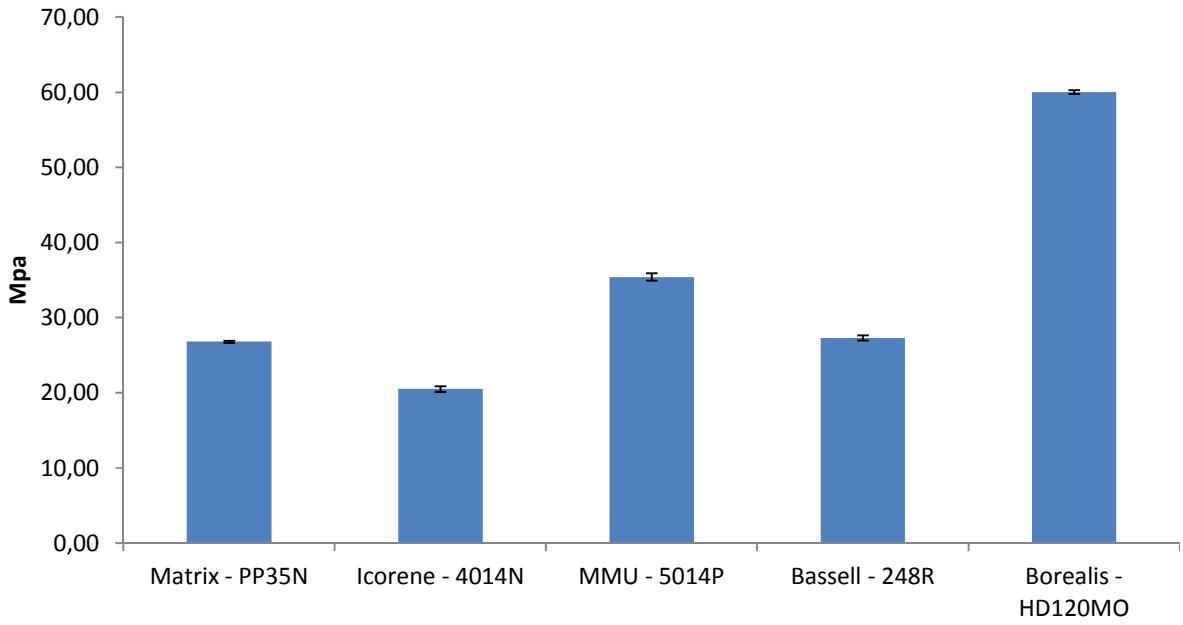


Figure 5.13: Graphic illustration of flexural yield strength of the various polypropylene materials tested (in MPa).

Both flexural modulus determined from the first 100 load – deflection data points (after the removal of any tail) and the flexural secant modulus between 0 and 1% strain gave sensibly similar data. This indicates that the load deflection data is linear over the strain range investigated. Such behaviour is quite typical of unfilled polypropylene.

Taking into account these results, it is clearly observed that the two homopolymers MMU – 5014P and Borealis – HD120MO have the highest stiffness which is consistent with their relatively high crystalline content. The two rotational moulding grades have lower stiffness which is a manifestation of their lower crystalline content. Bassell – 248R a PP copolymer on which some rotational moulding grades of PP are based, has similarly low stiffness (and crystalline content).

5.1.5.2 Tensile Properties

The following parameters are reported from the tensile testing data:

1. Young Modulus.
2. Secant Modulus.
3. Strain at Yield (Elongation at Yield (%)).
4. Tensile Strength or Yield Strength. Both coincide in this case.

Table 5.6: Results of the results of Young's Modulus (provided by Hounsifield Q-mat and at 0.3%), Tensile Strength and the crystalline content

Sample	*Hounsfield Q-mat Young's Modulus (GPa)*	*Secant Modulus (GPa)*	*Strain at Yield (%)*	*Tensile Strength (MPa)*	*Crystalline content (%)*
Matrix - PP35N	1,2	1,2	7,0	22,0	35,5
Icorene - 4014N	0,7	0,8	15,1	20,1	23,8
MMU - 5014P	1,8	1,7	9,6	32,1	41,2
Bassell - 248R	1,1	1,2	11,7	25,7	29,0
Borealis - HD120MO	1,6	1,7	7,0	35,0	44,0

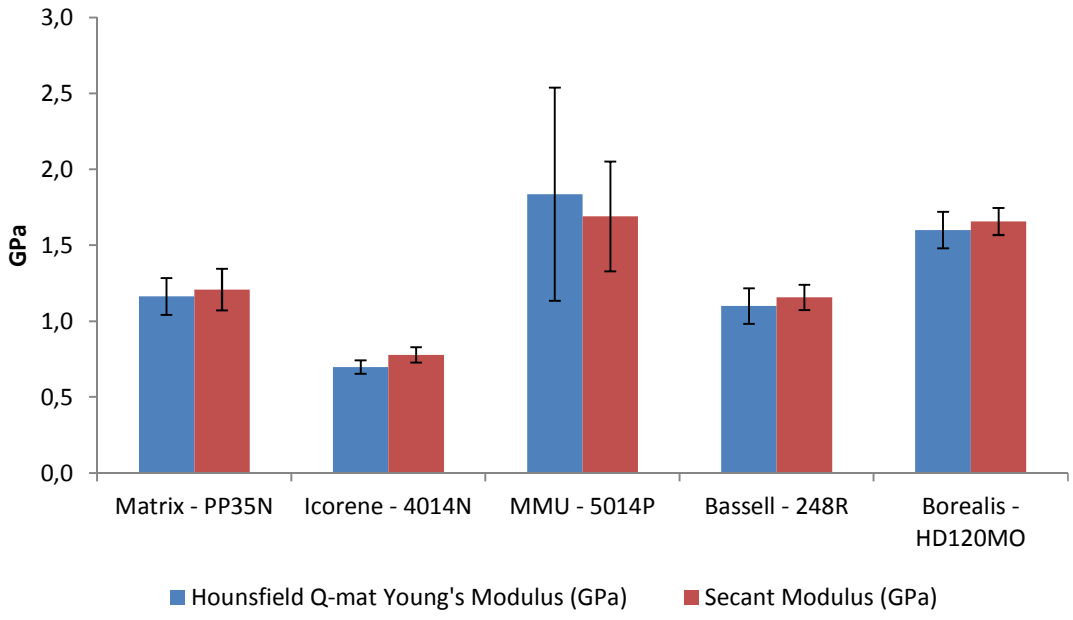


Figure 5.14: Graphic illustration of the Young's Modulus

Young's Modulus, which is a measure of stiffness of the samples within the linear region of their stress versus strain characteristics. As illustrated graphically in Figure 5.14 the PP with the highest stiffness are MMU – 5014N and Borealis – HD120MO which give values in the range expected for PP homopolymers. The other PP samples give somewhat lower modulus values which are consistent with their lower crystalline content. Arguably the lower values obtained (i.e. 0.7 GPa for the Icorene – 4014N) are not much higher than for high density polyethylene. This observation places a question mark over the merits of these materials in terms of stiffness enhancement (at room temperature) over polyethylene. The relationship between stiffness and crystalline content is represented in Figure 5.16, where it is evident that stiffness increases linearly with increasing crystalline content. This observation is entirely predictable as the amorphous regions in these PPs are in a rubber-like state at room temperature. The crystalline regions (which physically tie the chains together and constrain their movement) provide stiffness and strength; therefore the greater the crystalline content the higher the latter parameter will be.

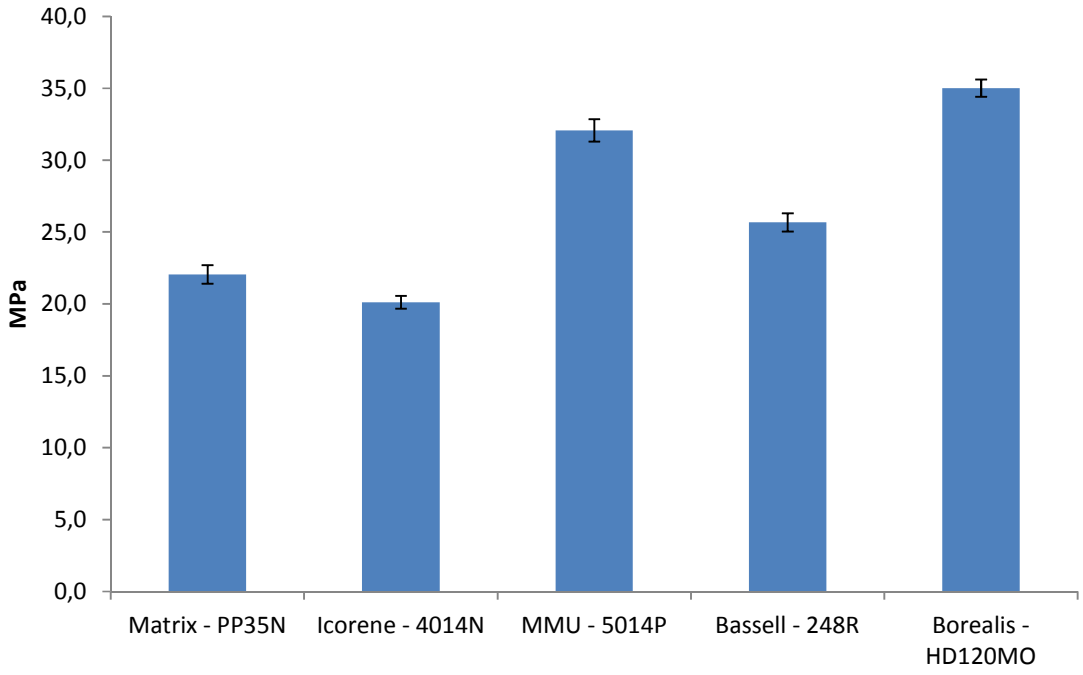


Figure 5.15: Graphic illustration of the Tensile Strength (stress at yield) of the various polypropylene materials.

The tensile strength data also generally goes hand in hand with crystalline content with the two homopolymers giving values between 32 and 35 MPa and the copolymer/blends giving lower values related to the amount, type and distribution of comonomers present.

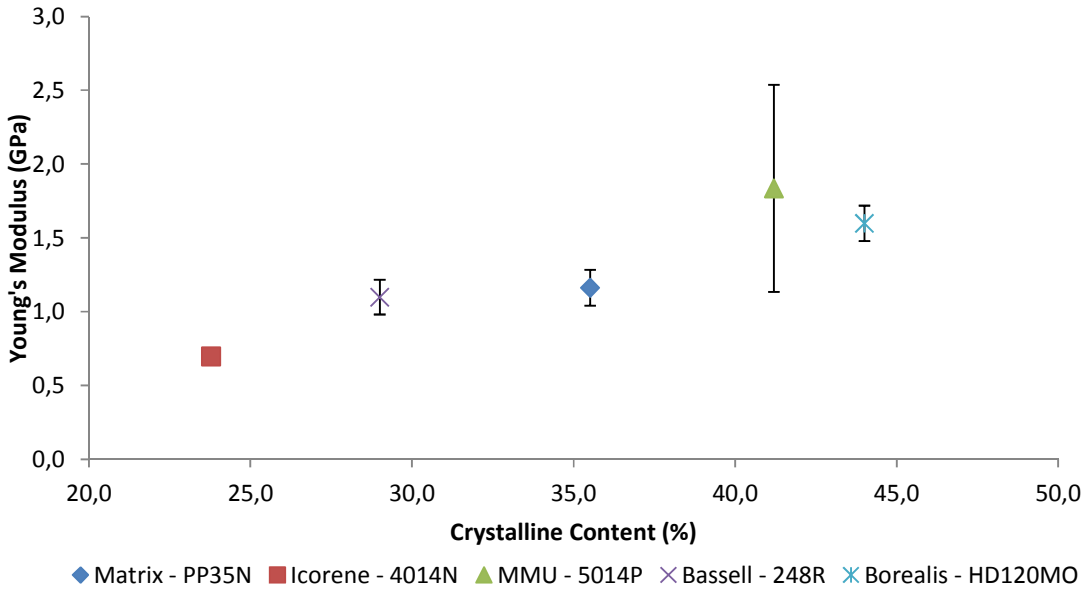


Figure 5.16: Illustration of the Young's Modulus v the crystalline content of each sample.

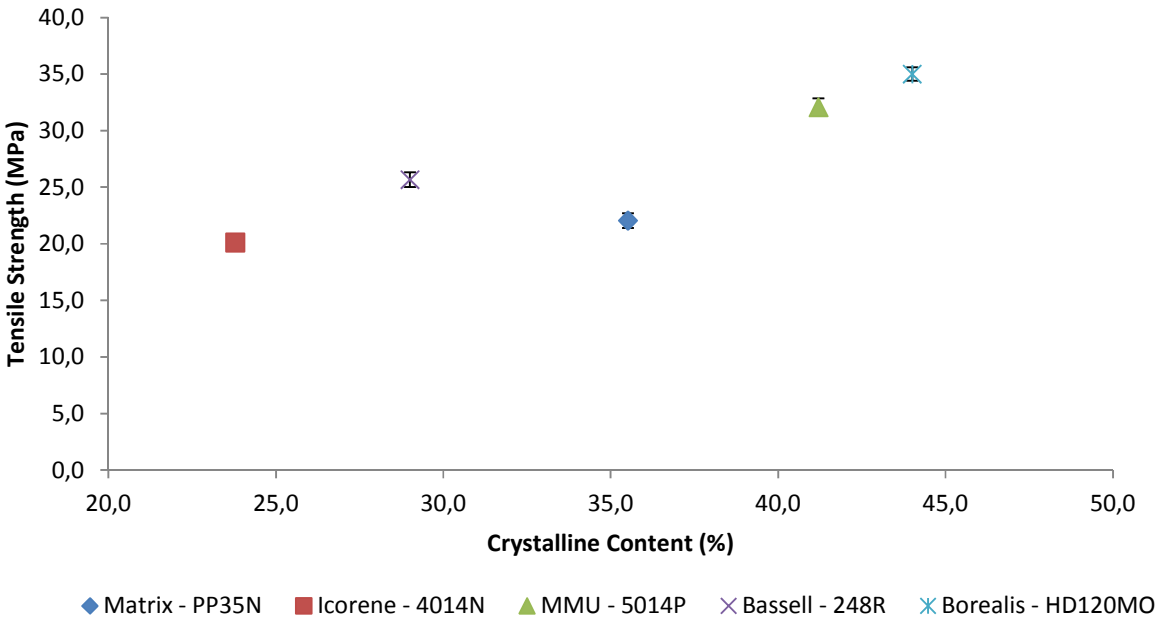


Figure 5.17: Illustration of the Tensile strength v the crystalline content of each sample.

5.1.5.3 Charpy Impact Strength

Impact tests are done to measure the resistance to failure of a material to a suddenly applied force. The test can measure impact energy or the energy absorbed prior to fracture. Impact strength is defined as a measure of the work done to fracture a test specimen. When the striker hits the specimen, it absorbs energy and it begins a plastic deformation at the notch. When the specimen cannot absorb any more energy, the specimen fractures. Tough materials can absorb a lot of energy, while brittle ones tend to absorb very little energy prior to fracture.

Despite the method used for notched and unnotched Charpy impact test being the same, more energy in necessary for the unnotched one, as is indicated in the table above. The behaviour of the samples in the notched Charpy tests has been analysed for years and the physical interpretation of the test is clear. However, the physical interpretation and behaviour without an existing notch is not straightforward.

Table 5.7: Results of the Charpy tests (notched and unnoteched) and the crystalline content of the samples.

Sample	*Notched Charpy Test Absorbed Energy (kJ/m$^{2)}$*	*Unnotched Charppy Test Absorbed Energy (kJ/m^2)*	*Crystalline Content (%)*
Matrix - PP35N	10,5	285,8	35,5%
Icorene - 4014N	10,9	235,4	23,8%
MMU - 5014P	5,2	83,1	41,2%
Bassell - 248R	8,9	168,6	29,0%
Borealis - HD120MO	5,4	82,0	44,0%

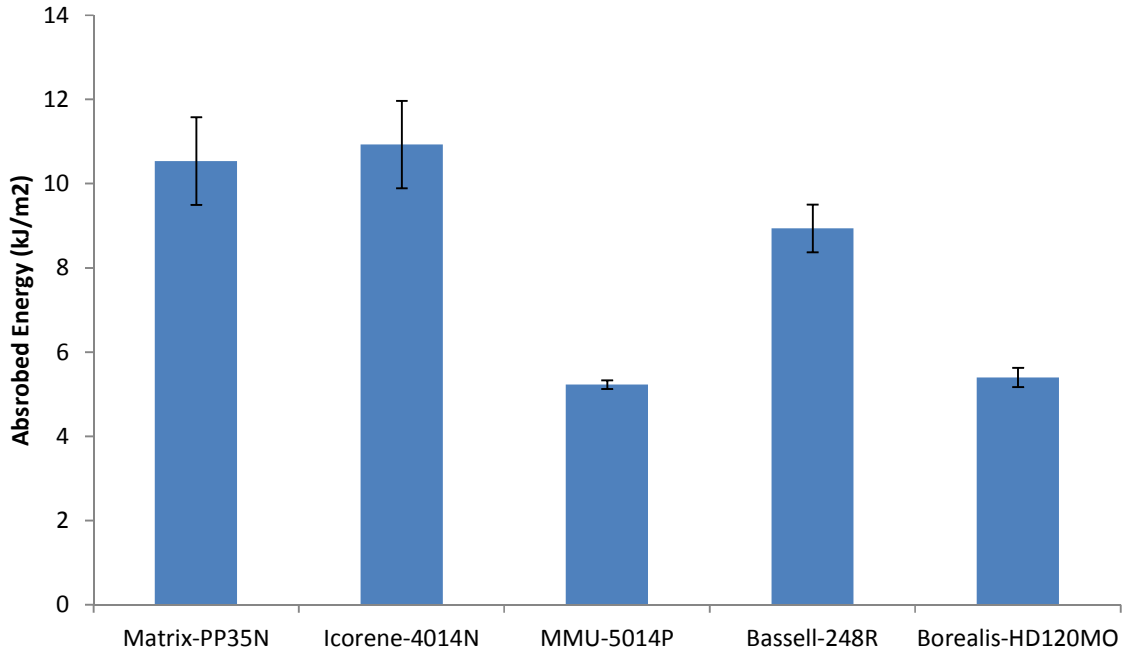


Figure 5.18: Graphic illustration of notched Charpy impact test and the standard deviation of each of the polypropylene materials investigated.

The two homopolymers, MMU – 5014P and Borealis – HD120MO, give similarly low values of notched Charpy impact strength due to their similarly high crystalline content. The copolymer/ blends have about double impact strength of the homopolymers and when experimental error is considered they are sensibly identical under these conditions, though the Bassell – 248R appears to be the poorest of the series.

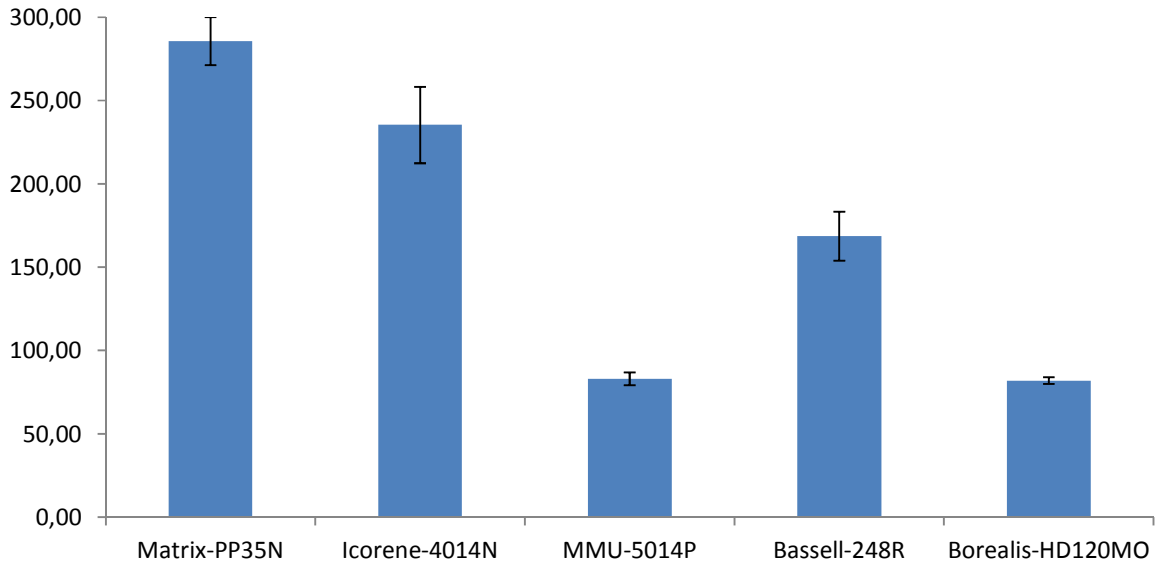


Figure 5.19: Graphic illustration of un-notched Charpy impact test and the standard deviation of each of the polypropylene materials investigated.

For this series of materials, the un-notched impact strength data is more discriminating between the copolymers/ blends, whilst the two homopolymers give similarly low values. Of the copolymers/ blends, the two samples formulated for rotational moulding (Matrix – PP35N and Icorene – 4014N) give the highest values of the un-notched impact strength with the Matrix – PP35N giving the highest performance. The Bassell – 248R a copolymer which is a component in some rotational moulding grades of PP, performed less well than the dedicated formulations, indicating that development work of the former has paid off.

As the amorphous regions of the materials are in rubber-like state at room temperature, it reasonable to surmise that impact strength will reduce as crystalline content increases. Notched and un-notched Charpy impact strength is plotted against crystalline content in Figures 5.20 and 5.21, respectively. All the samples apart from Matrix –PP35N follow the trend. The fracture behaviour of the Matrix – PP35N has been modified such that its toughness is not dependent on the amorphous regions, another toughening mechanism is apparent here.

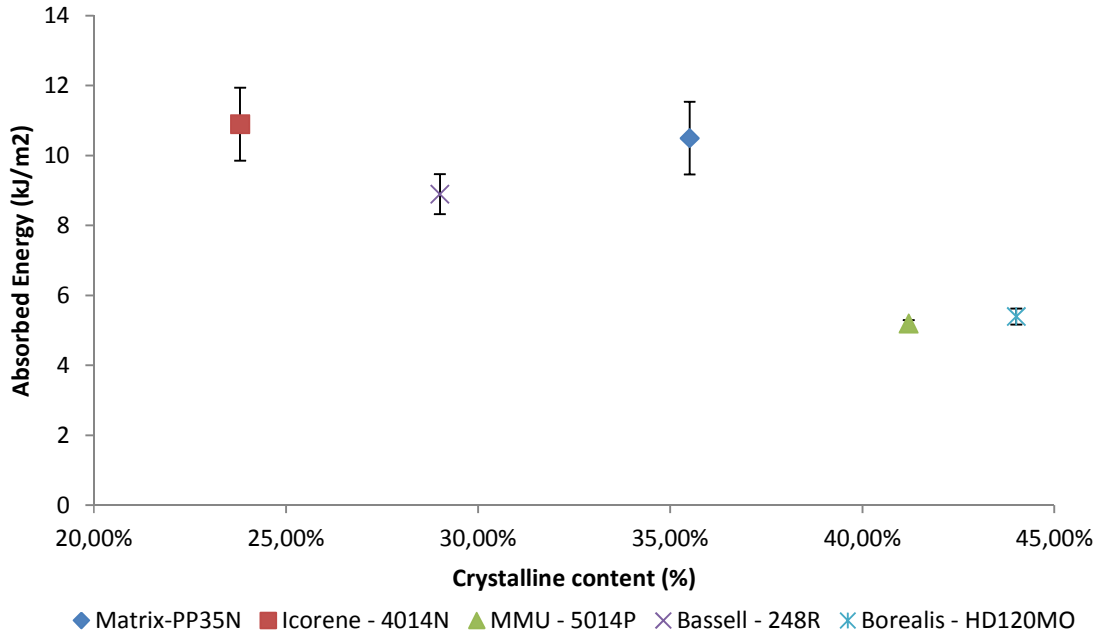


Figure 5.20: Graphic illustration of notched Charpy impact test v Crystalline content of each of the polypropylene materials investigated.

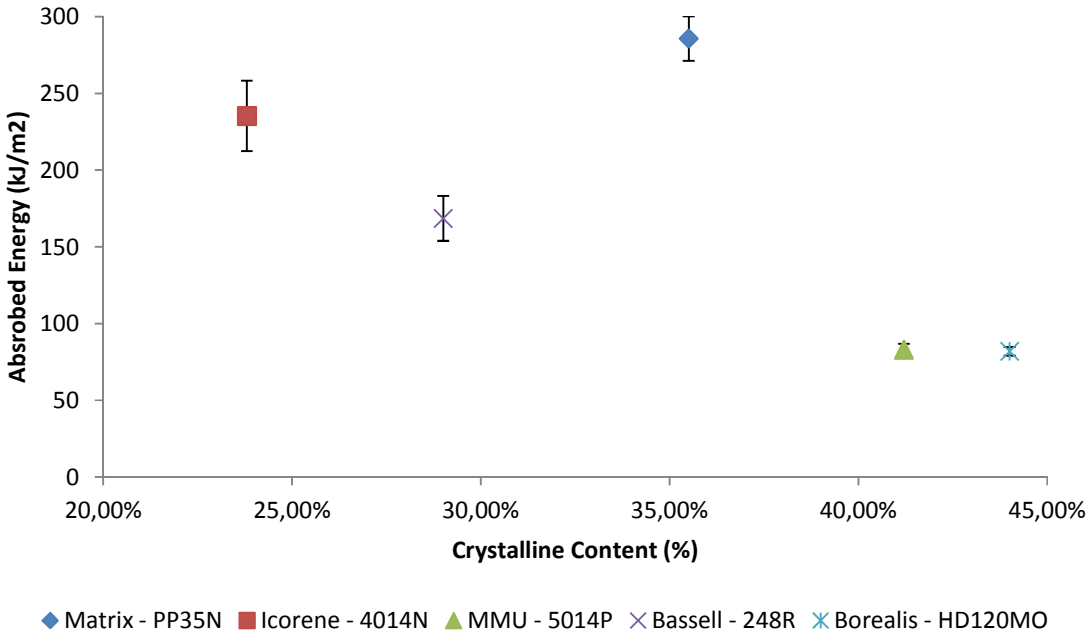


Figure 5.21: Graphic illustration of unnotched Charpy impact test v Crystalline content of each of the polypropylene materials investigated.

5.1.5.4 ARM Falling Dart Test Conducted at Ambient Temperature

Impact tests are widely used in the polymer and plastic industry and they are usually the first test done to characterise polymers. Because the use of only one impact test will have low accuracy and repeatability, more than one are usually done. In this case the test done is a dart impact test. This test could provide different ways of data analysis because the height and dart weight are related to the way of breaking as well as the velocity of the dart falling. Usually dart drop tests are utilised in the rotomoulding sector of polymer industry.

Table 5.8: Results of ARM falling dart at ambient temperature.

Sample	*Plaque Thickness*	*Dart Weigth (lb)*	*Height (ft)*	*MFE (J)*	*Brittle Failures (%)*
Matrix - PP35N	3	10	5,6	78,49	0%
	6	15	1,35	28,38	100%
Icorene - 4014N	3	10	5,55	77,79	0%
	6	15	7,25	152,43	100%
Bassell - 248R	6	15	0,95	19,97	100%

According to the results there are two observations that are important to mention. First of all, there is a big difference in failure mode between 6mm plaques and 3mm plaques. In the thickest ones the failures are 100% brittles failures. In 3mm plaques all the failures are ductile failures. Increasing sample thickness generally reduces toughness due to an increase in the fraction of material that is in the plane strain state. According the Von-Mises yield criterion, the plane strain (hydrostatic stress field) conditions increases the yield stress of a material and hence reduces its plastic zone size and reduces toughness [115-117]. The cooling rate of the thicker samples would also have been slower, resulting in a course spherulitic structure which is not conductive to high toughness due to the possibility of less efficient inter-spherulitic tying. An interesting observation is that to break 3mm plaque of the sample Matrix - PP35N more energy is needed than for the 6mm one. This result is slightly unexpected, though it may be because there were some voids in the 6mm plaque which may have acted as defects. As it is mentioned, thicker samples might have a reduction in the plastic fraction (amorphous region) and become surprisingly brittle. What it is evident is that the thickness of the samples is a factor that must be taken into account.

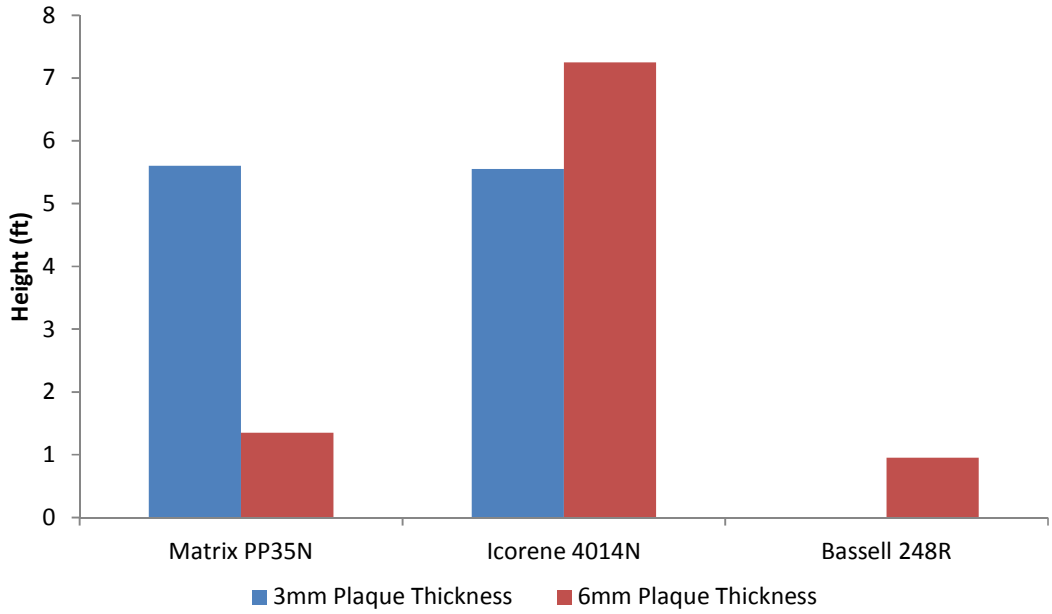


Figure 5.22: Graphic illustration of the minimum height needed to break the different plaques. Comparison of 3mm and 6mm plaques.

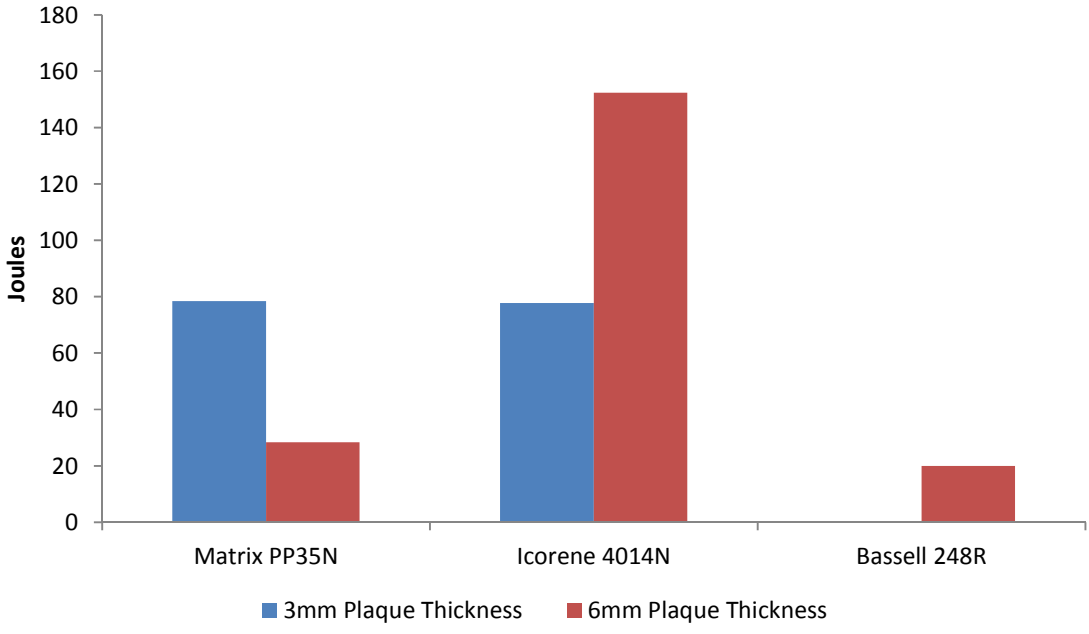


Figure 5.23: Graphic illustration of the energy required to break the different plaques. Comparison of 3mm and 6mm plaques.

5.1.5.5 Bulk Density and Dry Flow

Rotomoulding applications required special quality powder with a narrow particle size distribution. Good flowability is a prerequisite to achieve an optimum distribution of the material within the mould. This is the only way that uniform wall thickness of the produced mould is achieved. Good quality powders are those which are characterised by a narrow particle size distribution.

The bulk density of a powder is the ratio of the mass of an untapped powder sample and its volume, including the contribution of the interparticulate void volume. Hence, the bulk density depends on both the density of powder particles and the spatial arrangement of particles in the powder bed. Interparticulate interactions influencing the bulking properties of a powder are also interactions that interfere with the powder flow. In a free-flowing powder these interactions are less significant while in a poor flowing material there are greater interparticulate interactions.

Note: Material Bassell – 248R has not been tested because it is granulated

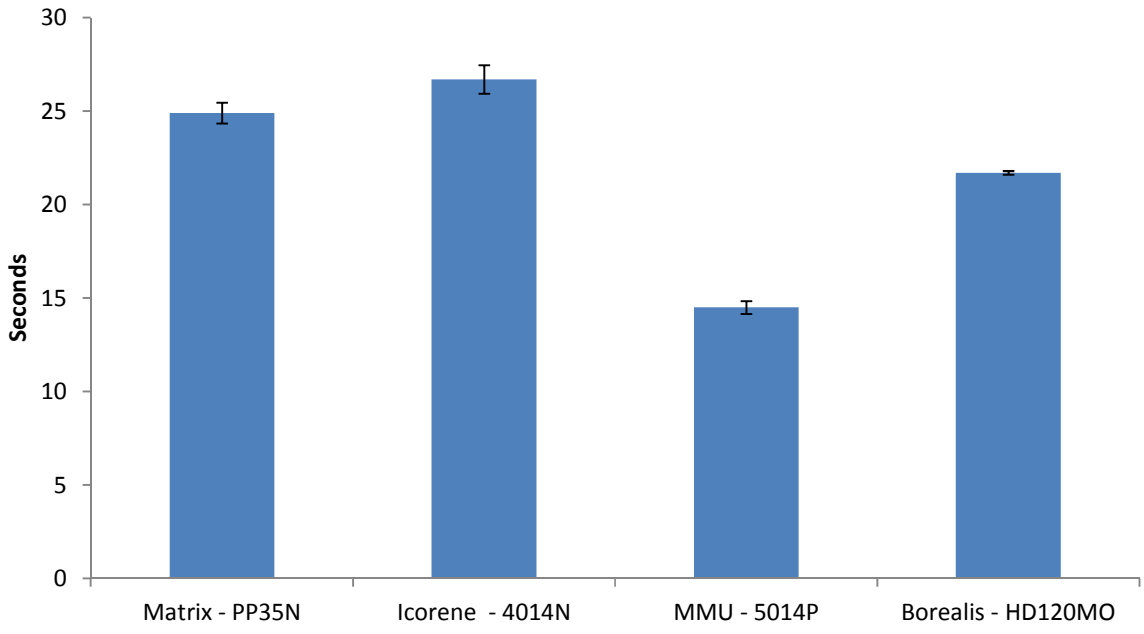


Figure 5.24: Graphic illustration of the dry flow of the various polypropylene materials investigated.

As figure 5.24 shows, the specimen with the lowest dry flow is MMU – 5014P, which means it had the weakest interactions between particles. On the other hand, Icorene – 4014N is the one with highest dry flow. Despite sample MMU – 5014P being by far the one with best dry flow, the other samples nevertheless flow with a reasonable and adequate time for rotomoulding.

Figure 5.25 displays the bulk density of the different samples which is related to the packing of the particles. As can be seen, MMU – 5014P has a slightly higher bulk density than the rest of the samples. However, all of them had an adequate bulk density to be rotomoulded. The bulk density at atmospheric pressure it is a useful parameter, but it supplies limited information. It is important to know how the bulk density changes with pressure and temperature because the compressibility of the materials determines the solid's conveying behaviour.

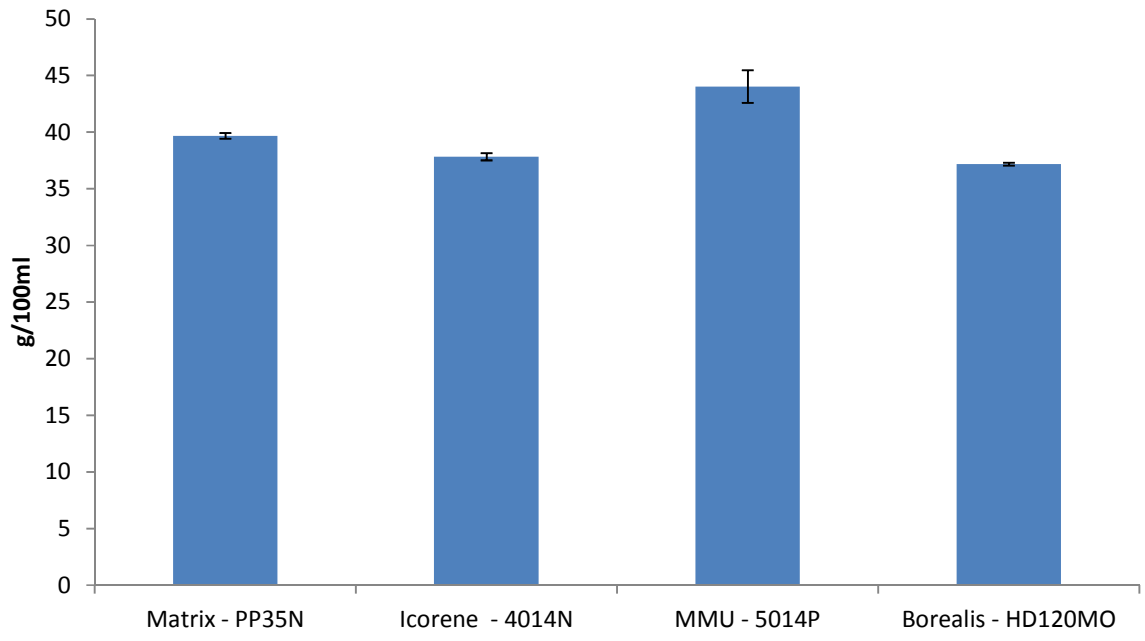


Figure 5.25: Graphic illustration of the bulk density of the various polypropylene samples evaluated.

5.2 IMPROVING THE MELT STABILISATION OF PP FOR ROTATIONAL MOULDING APPLICATIONS

After studying the competitive polypropylene for rotational moulding applications together with selected control references, this investigation continues with a study of the improvement of melt stability of PP for rotational moulding applications. After some discussion amongst the project team it was decided not to improve the best performing sample (Icorene – 4014N) in this regard, but rather monitor the extent of improvement in melt stability which could be afforded to the worst performing PP which forms the basis of certain rotational moulding PP formulations. The sample chosen was therefore *BASSELL – 248R*.

5.2.1 Stability and Synergism Studies

5.2.1.1 Stabilisation Activity of a Primary Antioxidant

The primary antioxidant chosen for the study is Irganox 1010 (I-1010). It will be added to the polymer matrix to see how the behaviour in terms of thermal oxidation is improved. The I-1010 was melt blended into the Bassell – 248R in a Thermo-Haake Rheomix 600 bowl for a period of six minutes, including a one minute plastification time, before which the I-1010 was added. After taking out the polymer, it was pressed manually and compressed with a 50 tonne press at 180°C for other ten minutes. The cooling step was done with a 50 tonne press connected to chillers at 15°C. To measure the thermal oxidation the samples were heated in an oven at 230°C. When the samples were taken out the carbonyl index was measured with the Nicolet Fourier Transform Infrared spectrometer fitted with a single bounce Smart Diamond attenuated total reflectance. The samples were taken from the oven periodically at intervals of 3 minutes.

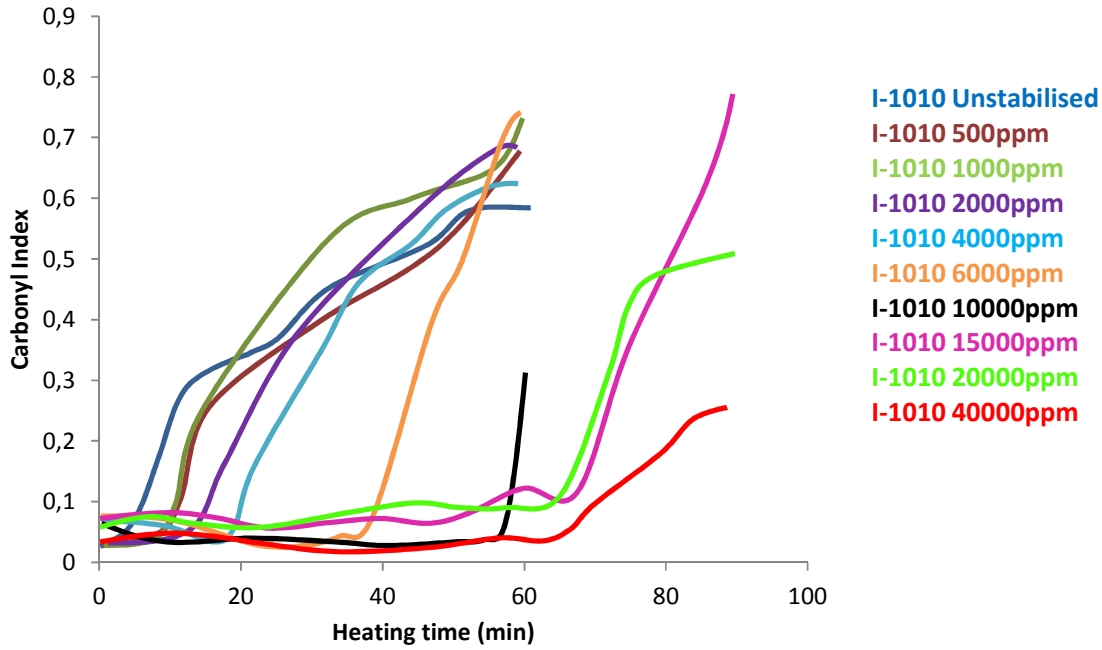


Figure 5.26: Carbonyl index of different Irganox 1010 concentrations in Bassell – 248R.

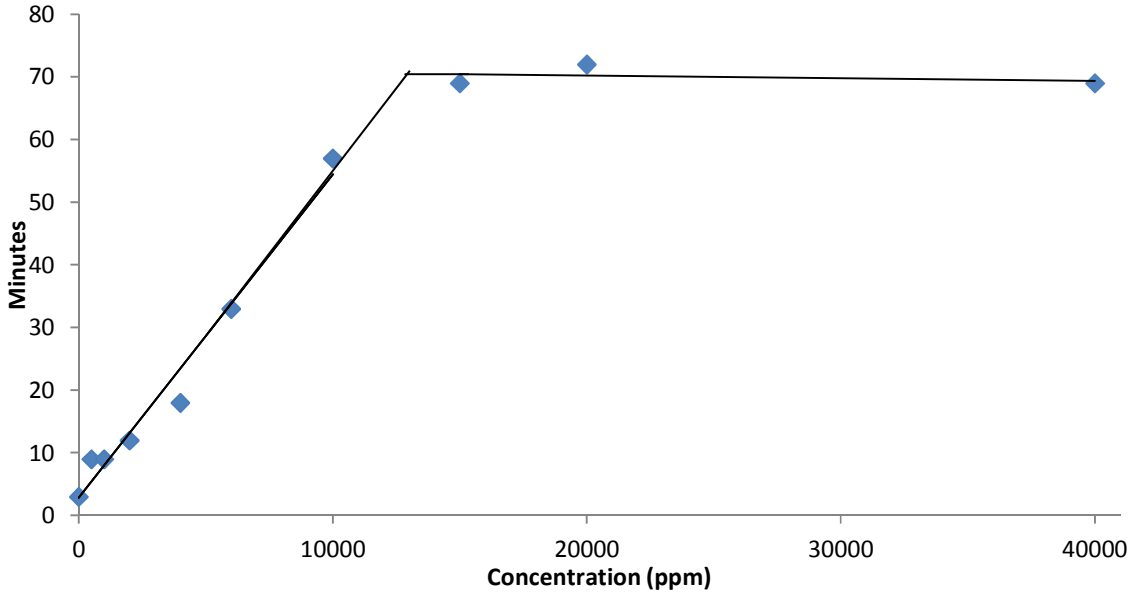


Figure 5.27: Time to onset of carbonyl growth at 230°C versus I-1010 level.

The longest induction times before carbonyl formation are obtained with higher concentrations, as can be expected. Figure 5.27 shows that at a temperature of 230°C induction

time to carbonyl growth increased linearly with increasing I-1010 level and then reached a limiting value of ca. 70 minutes at I-1010 levels beyond ca. 13250ppm (ca. 1.33 wt% on PP).

Rotational moulding rarely runs for this length of time, so the results obtained are promising to increase the thermal oxidation resistance of the PP. Usually rotomoulding of polypropylene lasts 30 minutes, so a 6000ppm concentration addition of anti-oxidant is arguably sufficient to ensure stabilisation during the process. Furthermore, the primary antioxidants are not cheap, so it makes commercial sense to limit the dosage if possible. Bearing in mind the level of stabilisation obtained, 6000ppm is reasonably economical. However, other rotational moulding studies [119] in which stability is investigated, use a lower concentration of antioxidant. Usually these dosages range from 400ppm to 1750ppm and combine primary and secondary antioxidants, however, they cannot stabilise the polymer more than 20 minutes at peak internal air temperatures lower than 230°C. In some studies [120], concentrations of 1% (w/w) (10000ppm) were utilised and the stabilisation obtained was clearly better but the economics of such high doses is open to question.

5.2.1.2 Synergism Studies between Primary and Secondary Antioxidants

As indicated in the literature review, thioether antioxidants work well with in conjunction with hindered phenolic primary antioxidants. However, other secondary antioxidants such as phosphites can also be utilised, as well as hindered amine light stabiliser (HALS). The latter do not only improve stabilisation against UV radiation, they can also improve resistance to thermal oxidation. From the data obtained during the first part of this thermal oxidative ageing study, it was decided to fix the total stabiliser concentration by mass to 6000ppm. A range of combinations were investigated in order to evaluate and compare the differences between stabilisers, as well as any potential synergism between these stabilisers. Data from this study will help to determine which combination of the primary antioxidant Irganox 1010 and secondary antioxidant will provide the best resistance against thermal oxidation.

As in the previous study, the samples were prepared using the Thermo-Haake Rheomix 600 mixing bowl and the electric press, (see section 4.2.1.1). In both cases, the polypropylene matrix is exposed to two thermal histories. The carbonyl growth was recorded using ATR-FTIR (as described in section 4.3.2).

Table 5.9: Stabiliser combinations and their induction time to carbonyl growth. The total concentration of antioxidant is 6000ppm.

Antioxidant	*Irganox 1010*	*Chimassorb944*	*Irgafos 168*	*Irganox Ps802FL*	*CIT*
Combinations	0%	100%			3
	12.5%	87.5%			6
	37.5%	62.5%			9
	50%	50%			9
	62.5%	37.5%			15
	87.5%	12.5%			24
	100%	0%			33
	0%		100%		12
	16.7%		83.3%		33
	33.3%		66.7%		33
	50%		50%		42
	66.7%		33.3%		42
	83.3%		16.7%		36
	100%		0%		33
	70%			30%	21
	75%			25%	24
	80%			20%	30
	85%			15%	21
	90%			10%	27

Synergism curves for Irganox 1010/Irgafos 168, Irganox 1010/Chimassorb 944 and Irganox 1010/Irganox PS802FL (in limited range) combinations are shown in Figure 5.28. It is immediately evident that the combination between I-1010/ I-168 shows strong synergism as other studies have shown [121].

As can be seen in Figure 5.28, in blue legend, the carbonyl induction time is increasing as higher Irganox 1010 concentrations are added to the polymer matrix. This indicates that there is a weak antagonism between these two antioxidants and the longer induction time is obtained as

a result the addition of primary antioxidant (Irganox 1010) amounts. Chimassorb 944 is anyway not an antioxidant formulated for increasing resistance against thermal oxidation, it is a hindered amine light stabiliser, so it provide better stability against UV radiation. It can provide some stabilisation when aldehydes and peracids are present, generally at low temperatures, and several works [56, 122] have proven that HALS could be used as long term stabilisers and even become more efficient than hindered phenolics. However, in rotomoulding high temperatures are used and C944 is not suitable for this application because the antagonism between HAS and phenolic antioxidants has already been proof in many works. So, the results obtained are not unexpected [123].

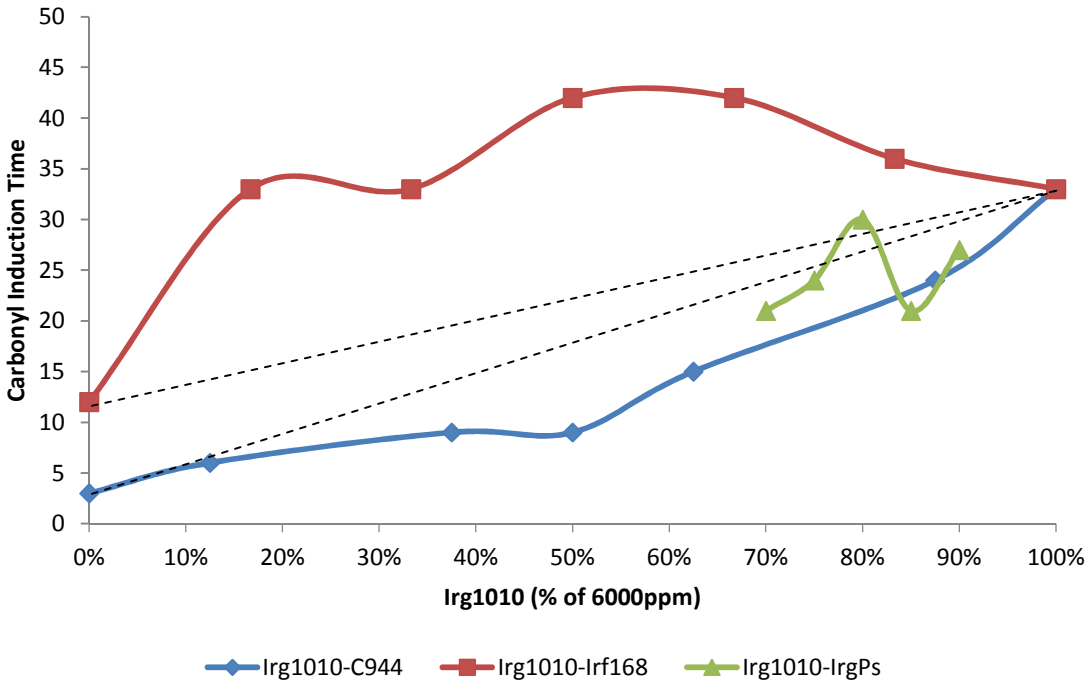


Figure 5.28: Carbonyl induction time (230°C oven ageing) of the different antioxidant combinations. The total amount of antioxidant added to the polymer matrix is 6000ppm and the graphic is expressed in % of Irg1010 in the combination

The data from Figure 5.28 with the red legend indicates that Irgafos 168 performs better that Chimassorb 944 to act synergistically with the primary antioxidant Irganox 1010. The optimum ratio under these conditions appear to be at approximately 60% I-1010/ 40% I-168. However, at 20% I-1010/ 80% I-168 combination also provides a reasonable stabilisation, and it will be

economically cheaper than the other two options due to the fact that phosphate antioxidants are cheaper than hindered phenolic ones.

Based on reference [6], a study of polypropylene stabilisation with Songwon 1010 and DSTDP (Irganox 1010 and Irganox Ps802FL (sulphur based thioester, secondary antioxidant) in this case) was conducted. Only five combinations were analysed. In the study mentioned, the best stabilisation is provided by the combination of 80% S1010 and 20% DSTDP. However, the study is more focused on long term thermal stability and it used 4000ppm concentration by mass while this is applied to rotational moulding applications. Therefore, the combination 80% I-1010/ 20% I-PS will be tried as the entry point formulation. As can be seen in Figure 5.28 with the green legend, the best stabilisation is provided by the 80% I-1010/ 20% I-PS combination. However, it is also possible that this combination shows weak antagonism, to be completely sure more measurements have to be done. Considering an overall view of the three secondary antioxidants, Irganox Ps802FL is not the one which provides the highest stabilisation against thermal degradation. This observation is not unexpected, due to thiosynergists beginning to lose their efficiency appeal above 160°C. As a conclusion, phosphites would be the best synergists with primary phenolic antioxidants.

5.2.1.3 Controlled Release Studies

The physical loss of the stabilisers from polymers results in the reduction of the stabilisation against thermal degradation. The encapsulation of molecules for controlled release has been studied and stabilisers can be adsorbed onto surface of silica gels and zeolites. Doping of the polymer matrix with silica which limits the mobility of the stabilisers can improve the stability of the polypropylene.

This study has only included the analysis of the primary antioxidant Irganox 1010 and the controlled release stabiliser silicate SD3128. Based on previous results the concentration of the

primary antioxidant will be 6000ppm. The same concentration is used for the controlled release silicate.

Unlike other studies of primary and secondary antioxidants, the materials which are the subject of this study only have just one thermal history because all melt blending was carried out using a twing screw extruder (Thermo-Prism TSE HC24, see Section 4.2.4) The TSE was used because larger amount of material were required for a rotational moulding processing stability study described in Section 4.2.1. Mixing and processing temperatures and pressures are mentioned in Chapter 4.2.4, Table 4.2. The sample was then introduced into an oven at 210°C and the carbonyl growth is measured with the FTIR-ATR spectrometer.

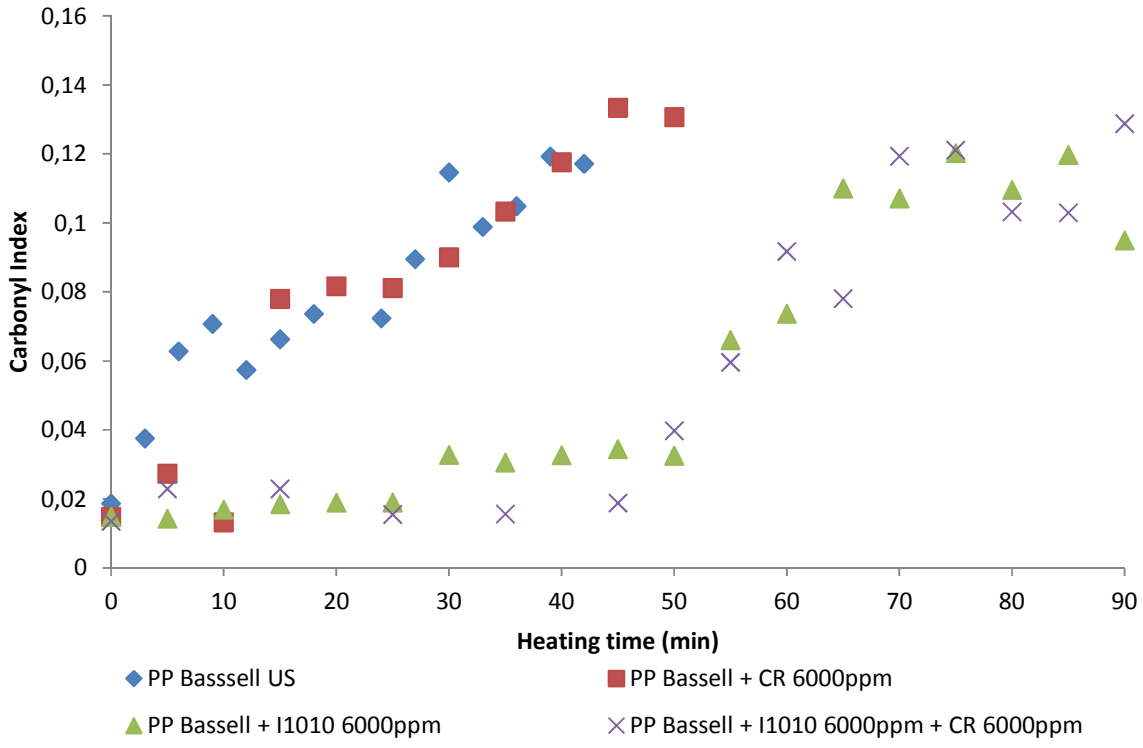


Figure 5.29: Carbonyl index versus oven agein time at 210°C for the samples indicated.

The retention of antioxidant molecules within the formulation during melt processing and during service of the component is an essential requirement for effective stabilisation. Grafting

of stabilising fuctional groups on to a polymer chain or a filler surface is a tempting proposition, however the effectiveness of stabilisation achieved by such methods is often less than expected. This is because the stabilising moieties are unable to move to where they are actually required [124, 125]. A preferred solution is to use normal stabiliser but control their release by adsorbing them on to an inorganic substrate with a very high specific surface area. Polymer stabilisation studies carried out at MMU have shown that a high surface area gel silica can control the release of stabilisers, most probably via controlled displacement mechanism [68]. However, for this study the SD3128 silica in combination with the primary phenolic AO I-1010 does not appear beneficial in terms of extending the CIT Figure (5.29), but may reduce the level of carbonyl growth before the onset of auto-oxidation. It may be significant that the CIT is unaffected by the presence of the silica and it may indicate that the antioxidant is restricted to the silica surface by adsorption unable to carry out its functions. In previous studies strong adsorption of I-1010 by silica actually reduced CIT. As mentioned earlier, it was considered that controlled release was achieved by displacement of a relatively weakly adsorbing stabiliser by a relatively strongly adsorbing one. This effect enhanced the synergy of the C-944/ I-1010 combination in polyethylene. Unfortunately the latter combination was not effective in the PP materials which form the basis of this study. The reason for this could be that antioxidant has not been diffused through the polymer matrix and it has been totally adsorbed by the silica limiting the antioxidants functions. The key idea of controlled release is that it provides a reservoir of additive that gradually releases under processing conditions to enable the reduction in amount of stabiliser.

In the rotational moulding processing stability study reported later in Section 5.2.3 the I-168/ I-1010 combination is investigated, both with and without the silica.

5.2.2 Nitrogen (N_2) Flush Tests

The study of the influence of replacing the air in the cavity of a rotational mould with nitrogen (nitrogen flushing) was carried out at GKN Aerospace in Portsmouth, using an industrial scale rotational moulding machine. The mould utilised was hexagonal prismatic in shape and described in Section 4.2.1. In contrast with the other studies to date, the polymers utilised were Matrix – PP35N and Icorene – 4014N, these were shown to have a relatively effective stabilisation package for rotational moulding. Bassell – 248R was not used as it is not representative of the best available rotational moulding grade PPs, at least in terms of processing stability.

The nitrogen flushing was carried out at a flow rate of 25l/min at pressure of 0.15 Bar. In order to reduce oxygen concentration to an absolute minimum, flushing commenced before the charged mould was put into the oven. Only a set of four Icorene- 4014N mouldings were prepared in nitrogen. The oven temperature was set at 250 °C and the temperature was measured inside the moulds with a thermocouple linked to a PC based data acquisition system. Table 5.10 summarises the rotational moulding conditions.

It was observed that the Matrix –PP35N seems to have more pinholes defects.

Table 5.10: Rotational moulding conditions.

Material	***Target Temperature (°C)***	***Demoulding Temperature (°C)***	***Oven Time (min)***
Icorene - 4014N	160	162	13.47
	175	184	15.59
	190	191,5	13.47
	205	208	14.58
	220	218	19.44
	235	234	25.41
Icorene - 4014N + N_2	160	165	11.48
	175	185	12.50
	190	Not Done	
	205	209,5	15.58
	220	224	16.46
	235	233,5	18.21
Matrix - PP35N	160	176	10.33
	175	181	13.31
	190	193	13.18
	205	208	15.41
	220	22	16.30
	235	236	19.23

5.2.2.1 Carbonyl Growth Measurement

After the rotomoulding, specimens were cut with an electric saw and the carbonyl index was measured utilising the FTIR-ATR.

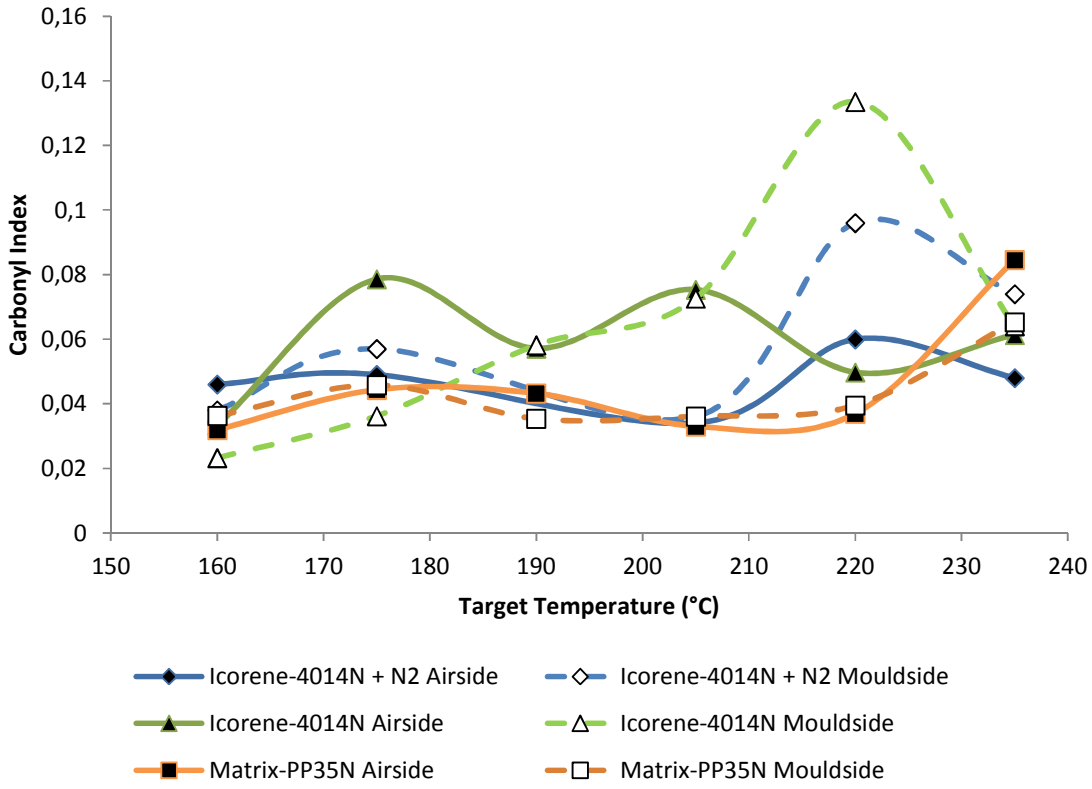


Figure 5.30: Carbonyl index for the airside and mouldside of rotomoulded samples.

Considering the Matrix –PP35N samples (no N_2) first of all, it is apparent that there was no significant difference between the carbonyl index values obtained for the mouldside and the airside. As the oven temperature (and also cook time) increases, there is no desirable rise in carbonyl index until ca. 220°C, beyond which a rise is observed with arguably the airside oxidising more rapidly. These observations indicate that the stabilisation package in Matrix – PP35N is relatively well resolved and performs well not only under OIT test conditions, but also under rotational conditions too. The Icorene – 4014N (no N_2) does not show the expected trend with the airside being more oxidised than the mouldside, in fact inspection of the general trends in the airside and mouldside data indicates that it oxidises at a faster rate which exceeds

that observed in the case of the Matrix – PP35N. Introduction of nitrogen certainly (in general at least) retards the rate of oxidation of Icorene – 4014N, but not to the extent anticipated. It may be the level of oxygen displacement was not as complete as expected. The quality of the ATR-FTIR spectra was also hampered by poor contact between sometimes relatively rough samples and the internal reflection element. In some cases attempts were made to improve contact by compressing the sample against polished steel surfaces in a KBr disc press.

5.2.2.2 Oxidation Onset Temperature

The onset of oxidation temperature (see Section 3.1.4 for method) of the airside of rotationally moulded samples was also determined to investigate differences between the levels of residual stabiliser Matrix – PP35N and Icorene – 4014N and the effect of the nitrogen flushing during moulding of the latter. OOT data is shown in Figure 5.31.

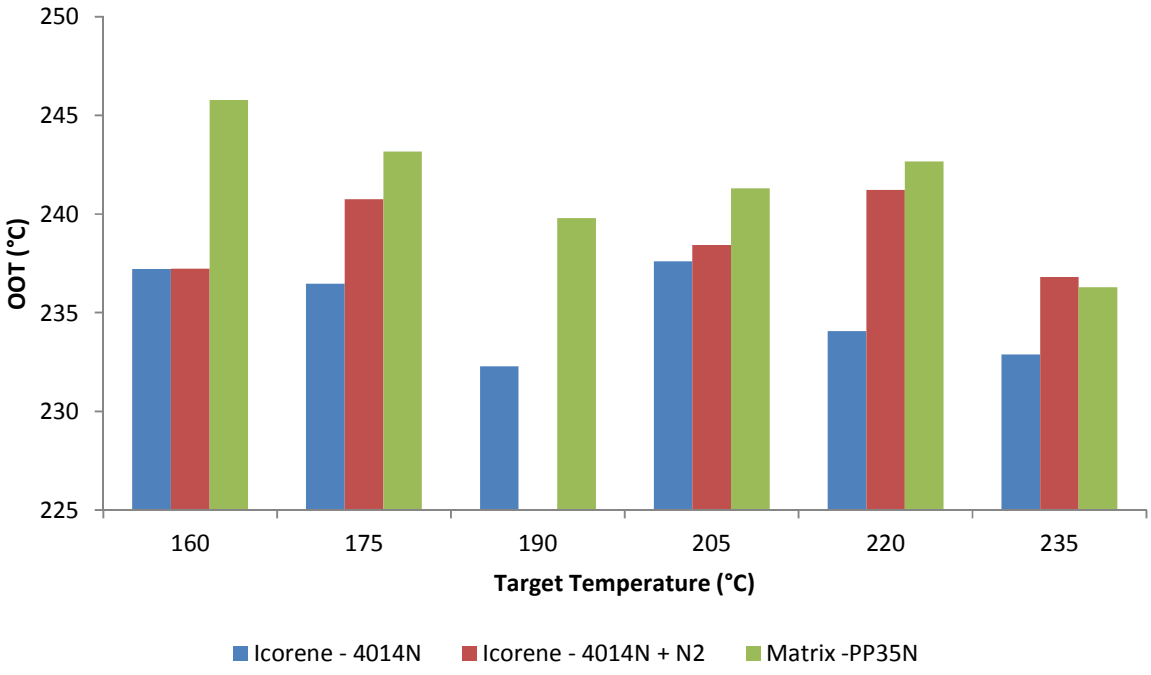


Figure 5.31: Graphic illustration of OOT of the rotomoulded samples measured by DSC

From Figure 5.31 it is again evident that Matrix – PP35N is the most suitably stabilised formulation examined in this study; OOT starts high at ca. 246°C and reduces to ca. 236°C at the

highest cook temperature/ time. Icorene – 4014N starts off reltively poorly (OOT 237°C), with OOT reducing to 233°C at the highest cook temperature/time. There is some variation in the OOT data for Icorene - 4014N but the OOT/ cook temperature - time trend is likely to be flatter than for Matrix – PP35N. A flatter trend may not be a bad feature as stabilisation at more extended cooking may be improved relative to Matrix – PP35N. Nitrogen flushing had no effect on OOT initially but as cook time/ temperature increased the benefit of nitrogen flushing became apparent leading to slower consumption of stabilisers and increased OOT.

5.2.2.3 Unnotched Charpy Impact Test

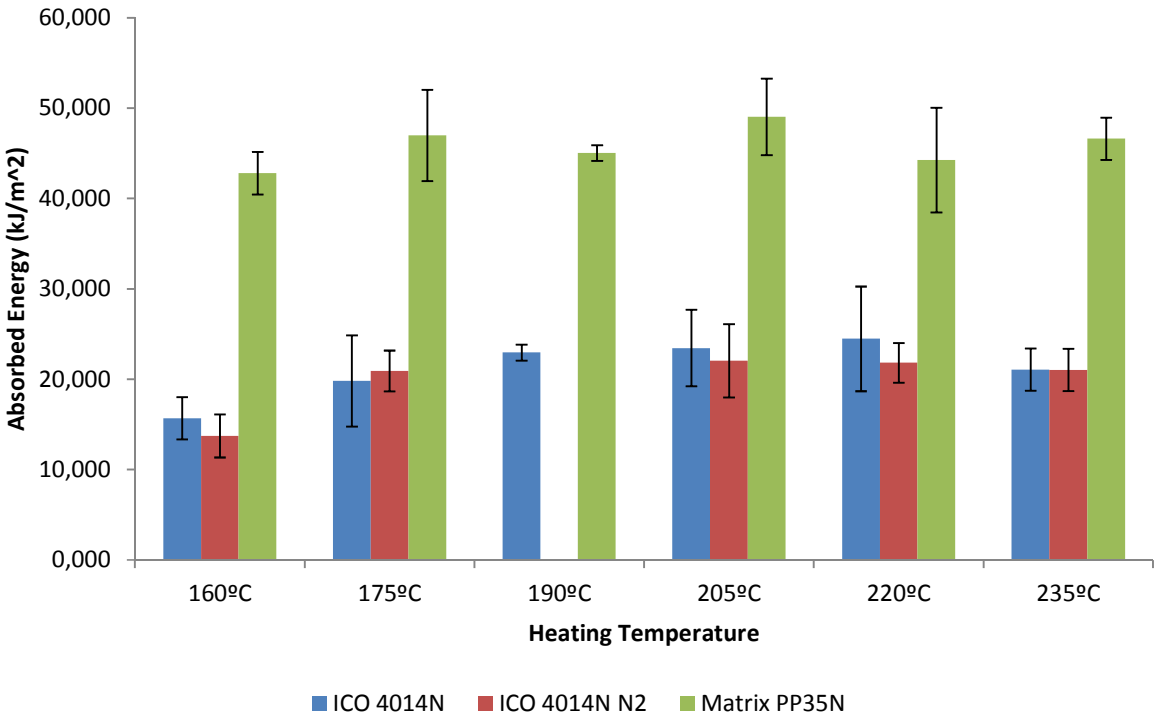


Figure 5.25: Graphic illustration of the impact strength of rotomoulded samples

Charpy impact test specimens (dimensions ca. 4mm x 10mm approximately in cross section with a 40mm span between the sample supports - see Section 4.3.3.3) were cut from the sides of the hexagonal prismatic test mould using a band saw. The impact test was done with a Zwick

5102 impact tester fitted with a 2J hammer. The mouldside was the side which was hitted by the hammer so, the airside was in tension during the test.

From Figure 5.25 it is evident that rotational mouldings formed from Matrix – PP35N were considerably better in terms of impact strength than those formed from Icorene – 4014N. Increasing cook time/ temperature made insignificant difference to the impact strength, an observation which further reinforced the view that the PP35N formulation performs adequately in wide range of temperatures.

In absence of nitrogen flush the rotational Mouldings formed from Icorene – 4014N had quite similar impact strength (considering experimental error) over cook time/ temperature range examined, though impact strength values around half those obtained for PP35N were observed. There is a weak indication that limiting impact strength was attained at 190°C. When experimental error is considered nitrogen flushing had no effect in impact strength, in fact in several cases the samples produced under nitrogen had marginally lower impact strength.

5.2.3 Bench-Scale Rotational Moulding Trials on Formulations Containing Controlled Release Substrate

Previous sections have discussed stabilisation routes for PP, for example via: the addition of primary antioxidants, studying the synergism between primary and secondary antioxidants and the addition of a controlled release subtrate. This section explores the bench-scale rotational moulding of formulations containing combinations of I1010 (4000ppm) and I168 (2000ppm), with and without the SD3128 controlled release substrate (added at 6000ppm) (this ratio of the two stabilisers was shown to provide the best stabilisation – see Section 5.2.1.2. Reference formulations include Irganox 1010 (6000ppm) (with and without SD3128 (6000ppm)) and unstabilised (with and without SD3128 (6000ppm)).

The samples were exposed to two thermal histories before being analysed. The formulations were pre-mixed and melt blended using the Thermo-Prism HC24 TSE (see Section 4.2.4, Table 4.2). After pelletizing, the mixtures were rotomoulded using the bench scale rotational moulding machine as described in Section 4.2.1. All the combinations were rotomoulded at five different cook times in order to monitor thermal oxidation via ATR-FTIR and the impact strength as a function of cook time. The melt flow rate of each pelletized formulation was measured in order to assess the extent of changes in average molecular mass during melt blending.

5.2.3.1 Melt Flow Rate

The MFR data is shown in Figure 5.26. Unusually for PP, the MFR of all the formulations (including the control with no additional stabiliser added) decreased by the same extent after melt blending. Due to the tertiary hydrogen, PP and PP rich formulation, usually undergo chain scission during melt processing [119,127]. This may be indicative of effective stabilisation (even in the control, perhaps because the copolymer (or blend) contains so much ethylene (or ethylene rich copolymer) that crosslinking just about overtakes chain scission. However, the addition of antioxidants and additives could induce to a substancial reduction of the MFI as M. Peltzer et al [126] have reported. This provides the indication that antioxidants are acting efficiently and that the polymer matrix is protected adequately.

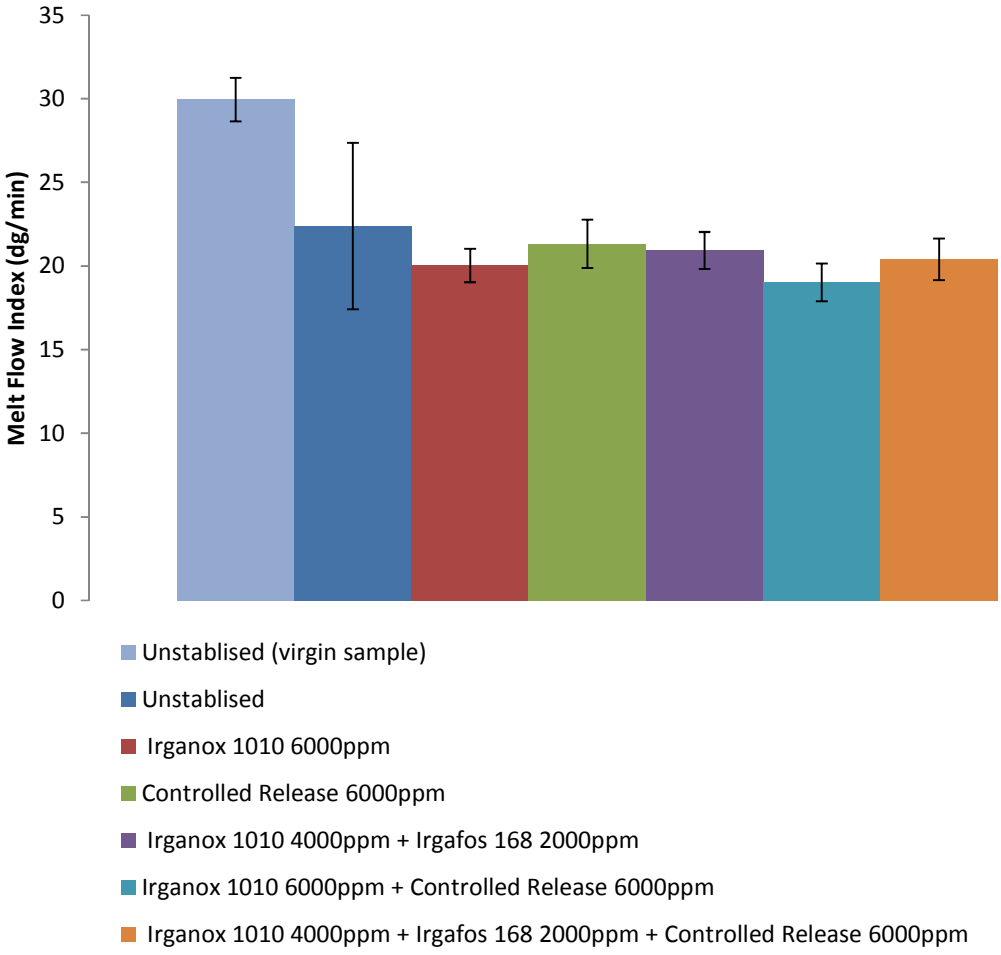


Figure 5.26: Melt flow index of the twin extruded samples with various combinations of additions.

5.2.3.2 <u>Carbonyl Growth Measurements</u>

Carbonyl growth was monitored using the FTIR-ATR analysis, similarly to the procedure outlined in previous sections. The samples were taken from the narrow sides of the mould. They have been cut manually with the band saw in order to get thin specimens, which provide good contact with the diamond internal reflection element of the ATR cell.

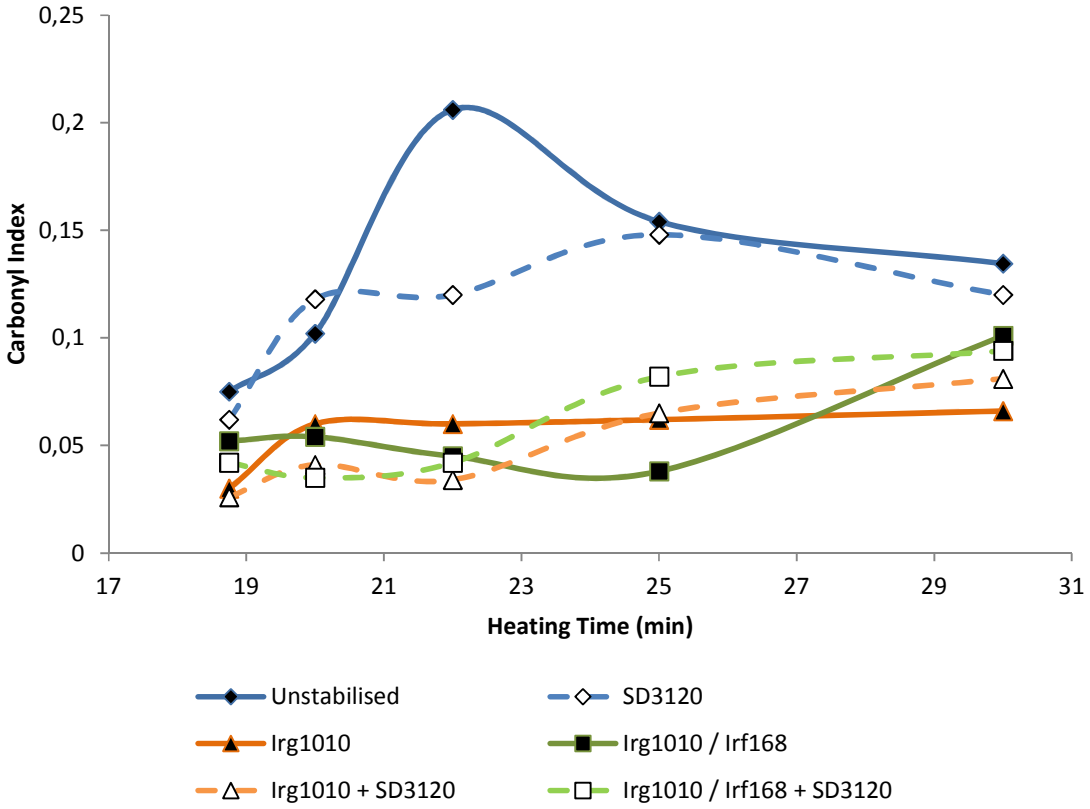


Figure 5.27: The carbonyl growth against time of the different rotomoulded combinations

Carbonyl index versus cook data for the bench scale rotational moulding process is shown in Figure 5.27. Considering the references containing no additional stabiliser first of all, it is evident that CI increases with increasing cook time with the increase being particularly rapid for the sample not containing the SD3128. Addition of I-1010 at 6000ppm provided very effective stabilisation; CI increased slightly to a limiting value at ca. 20 minutes cook time and did not vary over the cook time range studied. Combination of I-1010 with SD3128 resulted in initially improved stabilisation but after 25 minutes cook the data converged with, and then slightly exceeded, that for I-1010 alone. The reason for this could be due to silicas used to increase the crystallinity degree of the polymer, as many works have reported. Polymers with higher crystallinity degree will have a better behaviour against thermal degradation. Synergy of I-168 and I-1010 combination has been demonstrated earlier, however in this study was only marginally more effective than I-1010 alone and actually after ca. 27 minutes cook. Addition of

6000ppm SD3128 to this combination gave a very marginal improvement up to ca. 22 minutes cook and then gave a worse performance relative to when SD3128 was absent from the formulation. It is therefore apparent that the controlled release system does not function properly in this formulation at extended cook times, this may be due to the balance of interaction strengths between the SD3128 and the stabilisers being unfavourable, as some works have investigated [66] silica gels does not improve thermal ageing of PP when a unique antioxidant is added, and when synergistic antioxidant combinations are added it is dependent on the antioxidants structure.. Further work examining the heats of adsorption will have to be performed in order to explore this in the future.

5.2.3.3 <u>Unnotched Charpy Impact Test</u>

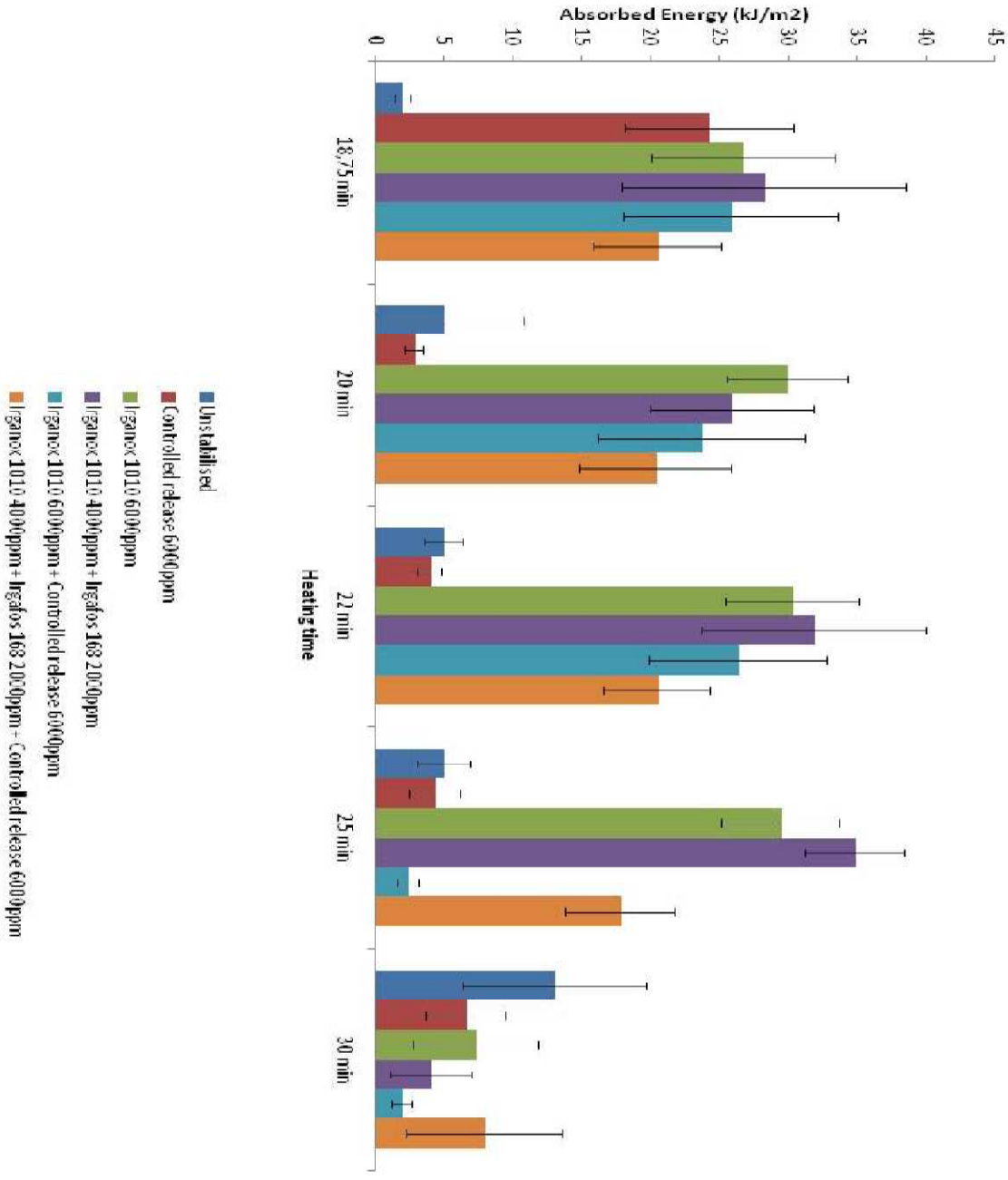


Figure 5.28: Graph showing unnotched impact strength of rotomoulded samples against the heating time.

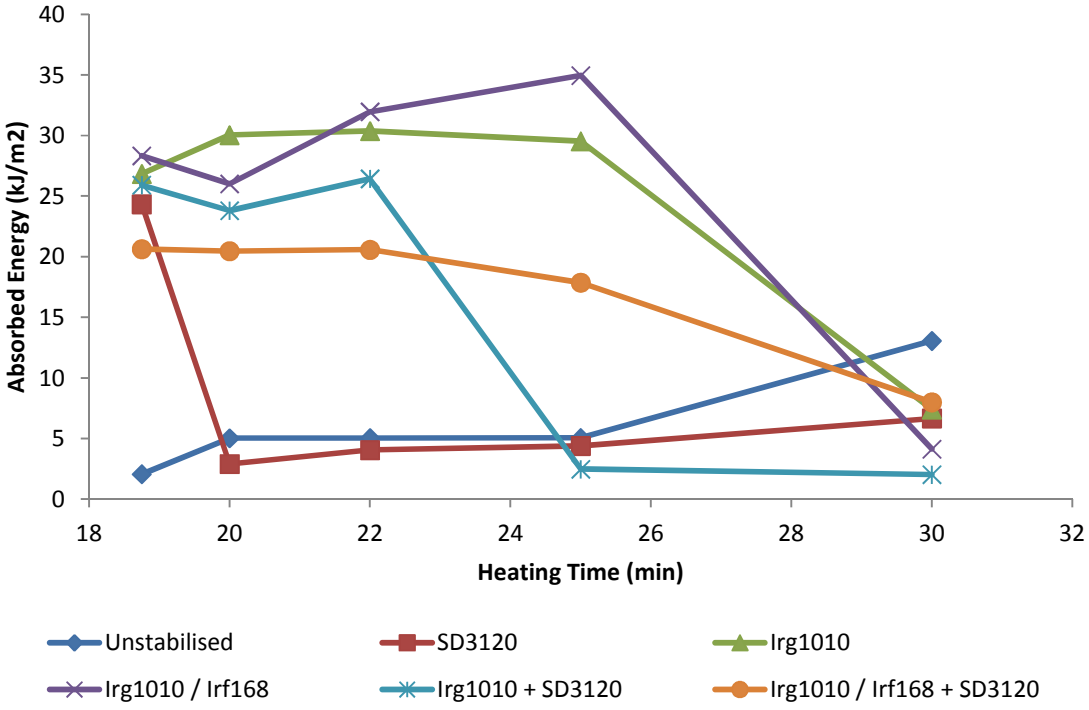


Figure 5.29: Graph showing unnotched impact strength of rotomoulded samples against the heating time.

Impact strength analyses were made with samples taken from the wide side of the moulds. The specimens were cut out using a band saw, due to the nature of this bench-scale rotational moulding system it was difficult to ensure consistent wall thickness between samples. Whilst sample cross sectional area is taken into account when calculating the impact strength, geometric factors cannot be accounted for and may have contributed to the large amount of experimental error. The trends are still nevertheless clear enough.

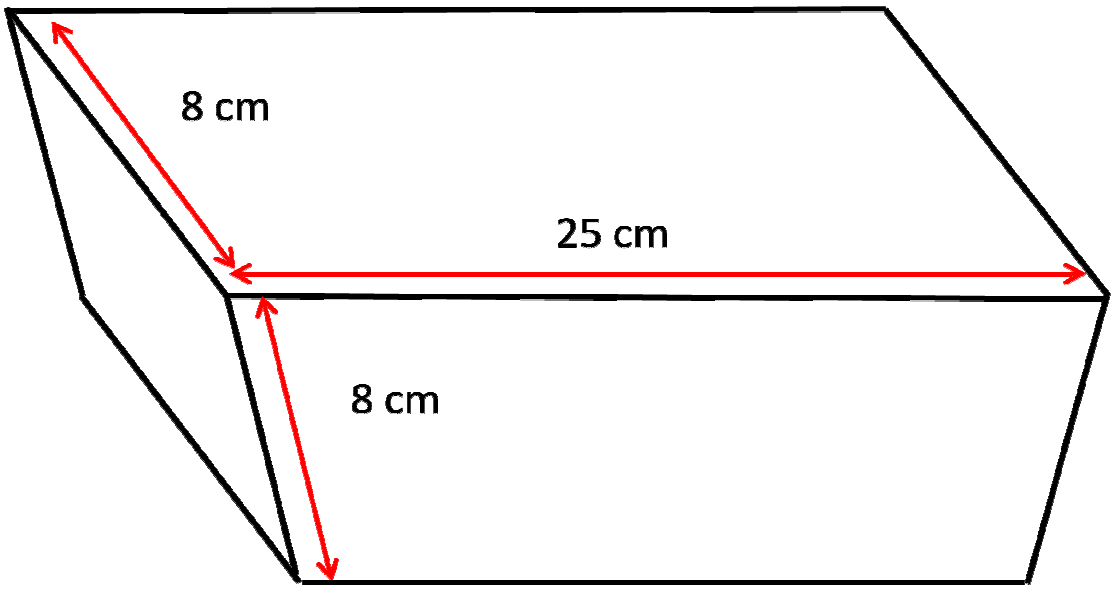


Figure 5.30: Diagram of the moulded used for the bench scale rotational moulding trials.

Considering the control sample with no added stabiliser first; it is evident that even after ca. 19 minutes cook significant degradation had taken place leading to a useless low impact strength (ca. 2kJ·m^{-2}), between 20 and 25 minutes cook there is arguably a small increase in impact strength (to ca. 5kJ·m^{-2}) and at 30 minutes the impact strength has rise to ca. 12kJ·m^{-2} (still a very poor value, but the best recorded at 30 minutes cook). These observations indicate structural changes occurring due to degradation which increase the toughness of the material. As the material is PP based copolymer or blend it there is some possibility of the PE rich component crosslinking and possibly forming bonds with the PP component.

The PP with SD3128 after ca. 19 minutes cook has an impact strength which is comparable with those of samples containing added stabiliser, this result is slight unexpected and requires further verification. However, it may indicate that the silica is controlling release of the existing stabiliser in the formulation. At longer cook time the performance falls to a level below that obtained by the control with no additional stabiliser added.

The sample containing I-1010 (6000ppm) performs well with an impact strength varying between ca. 26 and 30kJ·m^{-2} for cook times between 19 and 25 minutes. At 30 minutes cook

the added I-1010 has been consumed and impact strength plummets to ca. 7kJ·m^{-2}. Addition of SD3128 silica led to slight reduction in impact strength from 19 to 22 minutes cook, but at 25 minutes cooking impact strength fell to ca. 2kJ·m^{-2} and remained at the latter value at 30 minutes cook. This observation indicates that the I-1010 strongly adsorbed to the silica surface and was thus effectively removed from the system. There was no other more strongly adsorbing species present in the system to displace the I-1010 and I-168, gave better performance that I-1010 alone, but by a small margin. The blend tended to show its superiority at cook time of 22 and 25 minutes when impact strength values approaching 35kJ·m^{-2} were obtained. At 30 minutes cook, however, the impact strength feel sharply to ca.5 kJ·m^{-2} lower than for I-1010 alone. Addition of the SD3128 silica reduced impact strength to ca. 20kJ·m^{-2} at cook times from 19 to 22 minutes, at 25 minutes cook there was a small reduction to ca. 18kJ·m^{-2}. At 30 minutes cook, impact strength fall to ca. 8 kJ·m^{-2}. At extended cook time the presence of silica led to improved performance. A degree of controlled release behaviour may have been observed but the effect in this instance was not particularly significant or worthwhile.

6. CONCLUSIONS

This MSc thesis discusses the investigation of polypropylene into the use of rotomoulding applications. To carry out the project it has been split into two phases of investigation. The first phase focused on the analysis of the general properties of some commercial rotational moulding grades of PP in comparison with some other PP homopolymer grades and general purpose use grades. The latter phase studied the melt stabilisation of PP for rotational moulding applications and how it can be improved. This phase investigates the synergism between antioxidants to make the PP more suitable for rotational moulding and the use of a control release stabiliser which is an inorganic encapsulant.

After considering the results obtained during the analysis of the polypropylene grades, it is clear that different characteristics have been observed in the samples used.

Rotational moulding processes require a specific fluidity of the samples during the heating and cooling steps. Hence, specimens with a lower average molecular mass become suitable as this will deliver lower viscosity. From the results obtained in MFR test, Matrix – PP35 and Bassel – 248R are the most suitable samples with three times less viscosity than the PP homopolymers (MMU – 5014P and Borealis – HD120MO), which suitability is questionable.

The analysis of carbonyl growth measured by ATR-FTIR for the samples after being rotomoulded provided some curious results. Unlike PE when is processed in the same way, the rotational moulding grades (Matrix-PP35N and Icorene-4014N) show that the mouldside of these samples has been more oxidised than the airside for a significant cook period. However, the other two samples (Bassell-248R and Borealis-HD120MO) show PE – like behaviour, but the carbonyl index has increased more rapidly and to higher values compared to rotational moulding grades. From the results obtained it is evident that the two rotational moulding grades are well formulated and that the homopolymer and the injection moulding grade both require higher stabilisation against thermal oxidative degradation.

The crystalline structure plays an important role in polymer because many mechanical properties depend on it, thus the importance of the crystallinity studies. From the DSC studies some observations can be obtained. Both homopolymers have the highest crystalline degrees (MMU-5014P 41.2% and Borealis-HD120MO 44%) and higher Tm than the rest, which is usual for PP homopolymers. These observations are consistent with the results obtained with the XRD, both homopolymers provide sharp and intense peaks which means a higher Tm. Samples Icorene-4014N and Bassell-248R show a DSC pattern typical for β-PP structure which results in a lower Tm, as it is shown in the XRD patterns with low peaks. However, XRD do not show the typical β-PP peak at 16°, so the thin lamellar thickness and the low Tm of these samples might be due to a careful controlled copolymersation. On the other hand, Matrix-PP35N has a high crystalline content consistent with the sharp and intense peaks from the XRD pattern. Nevertheless, it shows a second peak in the DSC pattern which is probably PE. The formulation might contain a PP block copolymer or a plastomer type material. This will be reflected in some mechanical properties.

Degradation studies performed by DSC show consistency with carbonyl growth measurements via ATR-FTIR. Both rotational moulding grades (Matrix-PP35N and Icorene-4014N) show great performance against thermal oxidative degradation providing the highest OOT and the longest OIT. Therefore, it can be concluded these grades are well formulated for rotational moulding applications. However, PP homopolymers provide very poor results, not surprising for unstabilised grades. Bassell-248R provides better performance against thermal oxidation but still not as good as rotational moulding grades, so it would need more stabilisation to be employed for rotational moulding applications.

Mechanical properties were analysed with tests such as tensile strength and three points bend flexural strength tests, as well as Charpy impact strength and ARM dart falling test, which give information about the stiffness of the polymer and its brittleness. After observing the three point bend flexural test and tensile strength test, it is immediately evident that both homopolymers are the stiffest materials which correlate with their high crystalline content. The rotational moulding grades (Matrix-PP35N and Icorene-4014N) and Bassell-248R have lower

stiffness as they have lower crystalline content. However, at the time of analysing the tensile strength versus the crystalline content, it can be observed that Matrix-PP35N does not follow the trend, and it is less stiff than it should be for that crystalline content. This means it has been formulated carefully to decrease this property. As the amorphous regions of the materials are in a rubber-like state it is important to mention that impact strength decreases as crystalline content increases. This is because impact is spread more rapidly in crystalline regions. Hence, the samples which perform in a more brittle manner are both homopolymers, not surprising due to their high crystalline content. The rest of the samples double the impact strength of the homopolymers, with Matrix-PP35N having the best performance and Bassell-248R being the poorest of the series. Nevertheless, when impact strength is analysed against the crystalline content, Matrix-PP35N is out of the trend. So, the toughness of this material is not dependant on the amorphous region. It may be that an impact modifier has been included in the mixture. Dart impact tests show, that the thickness of the samples is important and must be taken into account, because excessive thickness could result in more brittle specimens due to the predominance of the plane strain state. Hence, these tests conclude that sample Matrix-PP35N has clearly the best mechanical behaviour and that is well formulated for rotational moulding applications.

Dry flow and bulk density measure the packing of the molecules and speed during flowing. Better packing will result in faster sintering of the polymer particles and reduce the time required for removal of air voids. A faster flowing polymer will result in a more homogenous spread of the powder around the mould and less difference in thickness of the mould walls. These parameters are of obvious importance for rotational moulding. According to the results, MMU-5014P is the material which has the best packing due to it having the finest particles. The packing of the other three samples is quite similar. Furthermore, MMU-5014P is also the fastest flowing, even though the rest of the samples also flow with an adequate speed for rotational moulding.

Taking into account the results obtained during the analysis of the different PP samples, it is clearly seen that Matrix-PP35N, which is formulated for rotational moulding, is the most suitable for rotational moulding applications. However, Bassell-248R was the brand chosen for the study of improvements of the properties with antioxidants, inorganic stabilisers and nitrogen flush. This brand is less suitable for rotomoulding, but it gives a wider range of variation for improvements and it will be easier to see the effect of the stabilisers. Anyway, it is important to remark that samples Bassell – 248R and Icorene - 4014N are a bit unusual PP grades as they have a high MFR and low crystalline content. This behaviour is quite different to the one observed in homopolymers (MMU-5014P and Borealis-HD120MO).

Investigation into the improvement of the melt stabilisation of the PP showed remarkable improvements to the thermal stabilisation of PP. The stabilisation studies via primary antioxidant (Irganox 1010, hindered phenolic) showed that its addition provides a linear increase of the carbonyl induction time until a concentration of 13250ppm. A larger concentration does not increase the CIT and it remains stable at approximately 70 minutes. This is a much longer thermal stabilisation than what is necessary for rotational moulding applications; hence a concentration of 6000ppm was the most suitable dose and was utilized in further studies. The synergism studies between primary and secondary antioxidants indicate that a combination of hindered phenolic anti-oxidant and phosphite anti-oxidant provides a synergistic effect. However, the combination of phenolic antioxidant and HALS or thioethers shows some weak antagonism. The best ratio of the combination between I-1010 and I-168 is about 60% I-1010/ 40% I-168 in a total concentration of 6000ppm. Despite this providing the longest stabilistation, the ratio of 1:5 it is also adequate for rotomoulding and more economical. The addition of the gel silica substrate SD3128 aims to reduce the active moiety of the antioxidants and thus, benefit the stabilisation of the polymer. However, for this study the combination of I-1010 with SD3128 does not appear beneficial in terms of extending the CIT. As conclusion, it can be said that insignificant adsorption of I-1010 happened onto the surface of the silica gel SD3128.

The studies of the effect of nitrogen flushing inside the mould and more specifically from the carbonyl growth measurements, indicate that the introduction of nitrogen retards the rate of oxidation but not to the anticipated extent. However, the displacement of the oxygen was not completed as expected. The analyses of oxidation onset temperature by DSC indicate that there is some benefit with the use of nitrogen flushing, especially at high temperatures became more apparent. The unnotched impact test for rotomoulded samples shows that differences between the different cook times/ temperatures have an insignificant effect on impact strength. Considering the experimental errors it can be concluded that there is no significant improvement with the addition of nitrogen, even though in some cases the samples moulded under nitrogen had marginally lower impact strength.

Before bench-scale rotational moulding trials were performed the MFR of the extruded samples was measured. Surprisingly, the MFR decreased which means that crosslinking overtook chain scission. In rotational moulding high MFR are preferred, so these results were contrary to requirements. However, the addition of antioxidants and additives could induce the reduction of the MFR, providing and indicating that the existing antioxidants are acting efficiently and adequately for rotational moulding applications. Carbonyl induction tests conducted for the bench scale rotomoulded samples show that specimens with no antioxidant have a rapid increase of the carbonyl growth. The best stabilisation is provided by the combination of I-1010/ I-168, which is consistent with previous tests, even though there is no big difference with I-1010 alone. The addition of SD3128 has no beneficial effect as the impact strength is lower. This test also shows that when antioxidants are consumed a dramatic decrease of the impact strength happens, clear evidence that when oxidation starts the mechanical properties suffer deterioration.

6.1 Further Work

Thermal stabilisation is one of the most important factors in rotational moulding. However, the moulds can be exposed to other degradation threats as they are likely to be outdoors. One of these degradation threats can be the UV from the sunlight. Hence, the moulds have to be stabilised with hindered amine light stabilisers and UV absorbers in combination with hindered phenolic and phosphites anti-oxidants.

Rotomoulding has a large range of applications and the products can often be used as fuel tanks in vehicles or as rain water collectors. The acidity of the water and the fuel chemicals can affect its properties and performance. Therefore, the study of stabilisation against chemical reactive compounds can also be an area of further investigation.

Apart from chemical threats, the moulds are also exposed to physical threats due to their applications. The improvement of the physical properties is necessary in order not to incur premature breaks. Some fillers, such as talc or calcium carbonate, could provide impact resistance, but they might affect thermal stabilisation. This could form a field of further future investigations.

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